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Geophysics. — *Maritime Gravity Survey in the Netherlands East Indies, tentative interpretation of the provisional results.* By F. A. VENING MEINESZ.

(Communicated at the meeting of June 28, 1930).

During the past year the Netherlands Geodetic Commission presided by Dr. J. J. A. MULLER has enabled the writer to make an extensive and detailed maritime gravity survey in the Netherlands East Indies and in the neighbouring parts of the Indian Ocean and the Pacific. This survey, comprehending 234 stations, has been made possible by the large spirit of cooperation shown by the Dutch Navy; for more than eight months the Commander of the Netherlands Indian Naval Forces, Admiral TEN BROECKE HOEKSTRA, has put a submarine, Hr. Ms. K XIII, at its disposal. Sincere thanks are due to him for granting this scientific enterprise and likewise to the captain of the K XIII, Lieut. G. MANTE, who took great pains in behalf of the investigation.

The small distance of the stations, mostly less than 50 or 60 miles, brought about an excessive number of divings, generally three or four per 24 hours of which always one or two occurred in night time. This meant much trouble and fatigue for the captain and the officers, Lieuts. K. VAN DONGEN, S. DEN BOEFT, C. VAN DER LINDEN, S. P. VISSER, A. DEUTEKOM and A. PLUIM, to all of whom the writer wishes to express his feelings of indebtedness.

Thanks are also due to the Commander of the Submarine Forces in Surabaya, Comm. VREEDE, to the Radio Service of the Netherlands East Indies for the sending twice per diem of a special rythmic time signal and to the Topographical Service of the N. I. Army for having these signals checked by their engineer, Ir. POLDERVAART, at the Bosscha Observatory at Lembang (Java).

The investigation has been carried out during three trips covering together 15600 miles. The routes and the stations are indicated on the accompanying map together with the stations which have already been occupied during previous voyages.

During the first trip of two months 105 stations have been observed in the Eastern part of the archipelago. This voyage was characterized by continuous rough seas. Near the small island of Serua one of the men was swept overboard, but he could be rescued without being the worse for his adventure. In the Arafura Sea the small lifeboat fastened to the afterdeck was severely damaged by the waves; it could be repaired at the Tenimber Islands.

During this trip the following islands and ports have been touched, though often only for a few hours; Sumbawa (Tjempi Bay), Flores (Endeh), Timor (Kupang), Tenimber Islands (Saumlakki), Key Islands (Tual), Aru Islands (Dobo), New Guinea (Arguni Bay), Banda Neira, Amboina, Halmaheira (Tobelo), Sangir Islands (Siao), Ternate and Batjan.

The second voyage of about one month round the island of Celebes gave opportunity for making observations at 65 stations; the boat touched at Kolaka, Buton, Gorontalo, Menado, Donggala, Balikpapan and Makassar; throughout the whole trip the sea has been calm.

The third voyage round the island of Sumatra took one month and a half; with the exception of a few days it was favoured by calm seas. During this trip 64 stations have been occupied. The following ports have been touched: Benkulen, Padang, Sibolga, Gunung Sitoli (Nias), Sabang, Belawan (Medan), Pulu Sambu (near Singapore), Palembang, and Tandjong Pandan (Billiton).

During the whole investigation echo soundings have been carried out by means of the Fessenden Sonic Apparatus for intersubmarine communication, with which the ship was fitted; the echo time was measured with an accurate stop watch indicating the 50th of a second.

After the first voyage new sonic receivers have been fixed up in the bottom of the ship and since then it has been possible to make also echo soundings at the surface of the sea; during the first voyage this could only be carried out when submerged.

The gravity observations have been made with the apparatus for maritime gravity research, which has given satisfaction during the whole research. No observation has been lost.

The writer has been continuously in contact with the oceanographic expedition of the "Willebrord Snellius" under leadership of Mr. VAN RIEL of the Meteorological Institute at De Bilt. This expedition is operating during the years 1929 and 1930 in the Eastern part of the archipelago; its numerous soundings are important for the reduction and for the interpretation of the gravity results. The soundings of the K XIII having miscarried in the Indian Ocean to the South West of the island of Sumba, the Snellius has made a special trip in this direction to supply the wanting data.

The principal reason for making the gravity research in the archipelago was the desire to get a complete and detailed gravimetric survey of one of the most extensive fields of tectonic activity of the earth; the frequency of earthquakes and numerous other indications make it probable that the tectonic stresses and movements are especially strong here. If therefore gravity can help to get an understanding of these processes, chances were good that the data obtained in this region would be valuable in this regard.

This viewpoint has been kept in mind when planning the routes and the stations. Where the direction of the tectonics could be surmised, the stations were arranged in profiles parallel to the direction of the forces as they might be expected, viz. perpendicular to the lines of folding or the rows of islands. In these profiles the stations have been chosen at the critical points of the topography and generally at distances not surpassing 50 or 60 miles. If the direction of the tectonic activity was doubtful, as for instance East of Celebes, it was attempted to cover the whole field by stations in such a way that the distances in any direction were not much greater than the above value.

For the greatest part the observations have already been computed provisionally and an approximate method for isostatic reduction has been applied to the results. In this way it is possible to give here an idea of the principal outcome of the research, but of course final conclusions cannot be given before the accurate computations and the isostatic reductions have been finished. However, the anomalies are so great, that it is improbable that the final reductions will materially change the principal features as they are mentioned in this paper.

The first important point which may be stated is that the archipelago shows abnormally large isostatic anomalies; apparently isostasy is not maintained where tectonic activity takes place, as is often supposed to be the case. This was not unexpected as isostasy means floating equilibrium of the earth's crust, and the presence of tectonic forces may be expected to disturb the equilibrium. It confirms the results which have been obtained in the archipelago during the voyage of 1926—'27, which likewise show great deviations of isostatic equilibrium

The second point, which is even more important and which has been quite unexpected, is that the deviations of isostasy do not show a clear parallellism with the topography of the earth's crust; they appear to be remarkably independent of it.

This makes it certain that the anomalies are not caused by a defective isostatic reduction. If the method of HAYFORD-BOWIE, which has been adopted for the provisional reduction, would not correspond to the actual distribution of the compensation, this will certainly cause errors in the anomalies, but these errors must show a definite correlation to the topography. This question can never produce the independent field of anomalies which has been found. Moreover, the anomalies are so big, that this alone would prevent thinking of this explanation. We have therefore to accept the anomalies as indications of real deviations of equilibrium of the earth's crust.

The principal feature is a narrow strip of strong negative anomalies, which runs through the whole archipelago and which is bordered to both sides by fields of positive anomalies. The strip has a breadth of about 100 miles; its course is indicated in the map. West of Sumatra it runs either over the islands or between the islands and the coast, South of Java it coincides with the submarine ridge between the two deeps running parallel to Java in the Indian Ocean, further to the Eastward the strip coincides with the row of islands: Timor, Tenimber Islands, Key Islands, Ceram but from here it leaves this row and takes a Northward course West of the island of Halmaheira over the Talaud Islands towards the Philippine deep. On the average the difference between the negative anomaly of the strip and the neighbouring positive anomaly is about 150 to 200 millidynes but locally it attains greater values; West of Halmaheira this difference amounts even to 430 millidynes. Over the Philippine deep it is less than further towards the South. This suggests that this deep is only a part of a much greater tectonic feature and that it is not a part where the tectonic forces are greatest 1).

It is of course not possible to predict with any certainty the further course of this strip which has been found to continue over more than 5000 miles. To one side it seems reasonable to expect the deeps East of Japan and South of the Aleutians to be connected with it and towards the other side it would be plausible to suppose that the negative anomalies in the Ganges plain are a continuation of this same feature. It seems a problem of first order importance to determine its further course.

Before going into the meaning of this strip of negative anomalies and the accompanying positive fields, some conclusions may already be drawn.

If we may accept these gravity disturbances to be the manifestation of the principal tectonic activity in the archipelago, they give indications about the course of the axes of folding. These indications differ in some important points from the actual views.

First it appears that the Timor-Savu arc continues towards the West in the submarine ridge South of Java instead of towards Sumba. The soundings made in these quarters by the "Willebrord Snellius" expedition seem to confirm this supposition.

Secondly the outer Banda arc (Tenimber Islands, Key Islands, Ceram) appears to continue from Ceram towards the North and not via Buru towards Celebes. The inner arc (Babber, Serua, Banda) instead of continuing in the Siboga ridge towards the South West, seems to bend likewise to the North; Buru, Sula Sanana and Majo might be expected to belong to it. The deep strait of Manipa between Ceram and Buru, the South East-North West strike in East Ceram and in Buru, the relative horizontal movements of these islands as surmised by BROUWER 2), all seem to be in good agreement with this course of the tectonic disturbance and with the theory mentioned below. A detailed study, however, of the relation of the surface geology of the archipelago to these results and to this theory will be necessary.

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1) An analogous result has been found for the Porto Rico deep during the gravity expedition of the U.S. Navy in the autumn of 1928. Here also the isostatic anomalies continue to the Westward in the prolongation of the axis of the deep. (These Proceedings Vol. 32, N⁰. 2, 1929).

2) H. ALBERT BROUWER, The Geology of the Netherlands East Indies, and other publications by the same author.

A second point which is worth while to mention is that the character of the gravity anomalies along the parts of the disturbance strip bordering on the Indian Ocean and on the Pacific is the same as for the part bordering on Australia and New Guinea. This seems to suggest that this latter continent does not play a leading part in the tectonic disturbance of the archipelago, although it is clear when we look at the map that its presence does affect the shape of the disturbance line.

Lastly it may be remarked that according to these indications it appears probable that the Alpine-Himalayan orogenic system does not continue towards New Guinea but that it bends towards the North and runs along the Eastern border of the Asiatic Continent. In other words the Pacific orogenic system seems to be the continuation of the Alpine-Himalayan system.

Coming now to the question what may be the origin of this strip of strong negative anomalies, it is clear that this origin is not deep-seated. This may be concluded from the fact that the transition from the negative towards the positive anomalies is generally of a sudden nature. A change of an amount varying from 100 to 430 millidynes is mostly found on a distance of about 100 miles. If the origin of the anomalies were seated at a depth greater than some 40 km., this mass distribution would have to be complicated and improbable in order to produce this surface effect.

On the other hand the independence of topography and anomaly field makes it equally improbable that the cause is situated in the surface layer of the earth's crust or that it is directly connected with it. It can for instance not be found in a partial or complete lack of compensation of the topographic features, because in this case there would be some correlation to the topography.

Neither is it probable that the cause may be found in the action of forces which are pressing down or pushing up the crust out of its equilibrium position, because the strip of negative anomalies coincides over a great part of its length with a row of islands or a ridge, while the positive anomalies are mostly found above deep parts. We would then have to suppose that the islands and the ridge are pressed downwards in order to explain the deficiency of mass corresponding to the negative anomalies and the deep sea parts must be supposed to be pushed upwards for explaining the positive anomalies. These movements are certainly improbable; if any movements might be expected, they would occur in contrary sense. So the writer thinks that this supposition, to which he felt inclined after former voyages when finding deviations of isostasy in tectonically active areas, must be rejected.

Carefully examining the matter it appears more plausible to assume that the strip of negative anomalies is caused by some abnormal accumulation of light surface material in a sub surface denser layer. This brings us to the hypothesis which in the opinion of the writer covers all the facts, that the cause is a downward folding of the whole earth's crust with the exception of a thin surface layer.

This surface layer folds upwards and in the long run forms overthrust sheets in the manner as has been stated by the geologists in the Alps and in other folded mountain systems. Its thickness is estimated at not more than a few kilometers while the main part of the earth's crust is thought to have a thickness of some 20 kilometers or more[1]).

The downfolding of this main part brings about the accumulation of light surface material in the crust which corresponds to the strip of negative anomalies.

This hypothesis is in harmony with the supposition of MOLENGRAAFF, BROUWER and numerous other geologists that the Indian Archipelago represents the first stage of a mountain folding process. It is founded on the Airy hypothesis of isostasy, which supposes that the isostatic compensation of a mountain system is formed by a root of lighter crust material embedded in the sima layer.

This root must come into being during the folding process and as it is many times more voluminous than the mountain system itself, it may be assumed that its formation is by far the principal feature of the phenomenon and that the surface folding is only a relatively small accompanying process. During the folding which is now going on in the archipelago, the root formation causes the strip of negative anomalies, which is the dominating feature of the gravity field.

The only important point in which this hypothesis differs from the actual range of ideas, is the fact that this main folding process has a less local character than the superficial folding of the upper layer. This appears to act more or less independently and often shows many parallel folds accompanying one downward fold, as for instance in the double Banda arc. In this way not every surface fold is accompanied below by a downward fold, while the prevalent view is that every fold develops its isostatic compensation exactly below it. Now, apart of the fact that the gravity results in the archipelago show that isostasy is not valid during the process, the hypothesis which is mentioned here, seems a reasonable one. The downward folding main part of the earth's crust is many times thicker than the surface layer and may therefore not be expected to undergo the same local foldings. Probably also this downward folding will not assume the same shape and overthrust or underthrust character as the surface folds.

Other reasons for the surface folds having a more capricious and intricate character, are the erosion to which part of the surface is exposed and the greater strength[2]) of the surface layer.

If the downward folding is not completely covered up by the surface folds, the downward movement of the earth's crust reveals itself by an ocean deep, as in this instance the Philippine deep or the Java deep. Probably the sea-side slope of these deeps may be regarded as a true image of the sloping of the earth's crust towards the downward fold, which is situated itself below the ridge bordering the deep on the land-side. This agrees with the situation of the strip of negative anomalies.

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[1]) It lies upon the surface to think that these layers are identical with those deduced by Jeffreys from the seismic data.

[2]) Definition of strength given by Jeffreys in "the Earth".

Another instance of the downward folding movement manifesting itself at the surface, may perhaps be found in the dip of the surface folds; the writer thinks that in the archipelago several of these instances may be found as e.g. in the outer Banda arc and in East Ceram; but a detailed treatment of these questions must be put off till the final results are available.

It may be expected that, as the folding process continues and the overthrust sheets of the upper layer are piling on, this packet is concentrated by the movement above the downward root. It is therefore clear that in the long run the phenomenon is tending towards isostatic equilibrium and that in this way the final stage of a compensated mountain system will come into being.

A point which will need an elaborate further study to clear up, is the question if the surface folds in themselves are in isostatic balance; this might be achieved by a local bending of the main crust layer under the weight of these folds. The uncertainty regarding this point makes the exact location of the principal crustfolding still slightly doubtful; a provisional study shows, however, that the error of the location can not be considerable.

The folding of the earth's crust must be caused by a strong tangential pressure in the earth's crust. This pressure may account for the fields of positive anomalies on both sides of the folding line.

If a part of the earth's crust is subject in one direction to a pressure d per unit of vertical cross-section, if the thickness of the crust is given by h and the earth's radius by R a simple consideration of the equilibrium of the crust shows, that the crust is subject to an upward force of an amount pro surface unit of

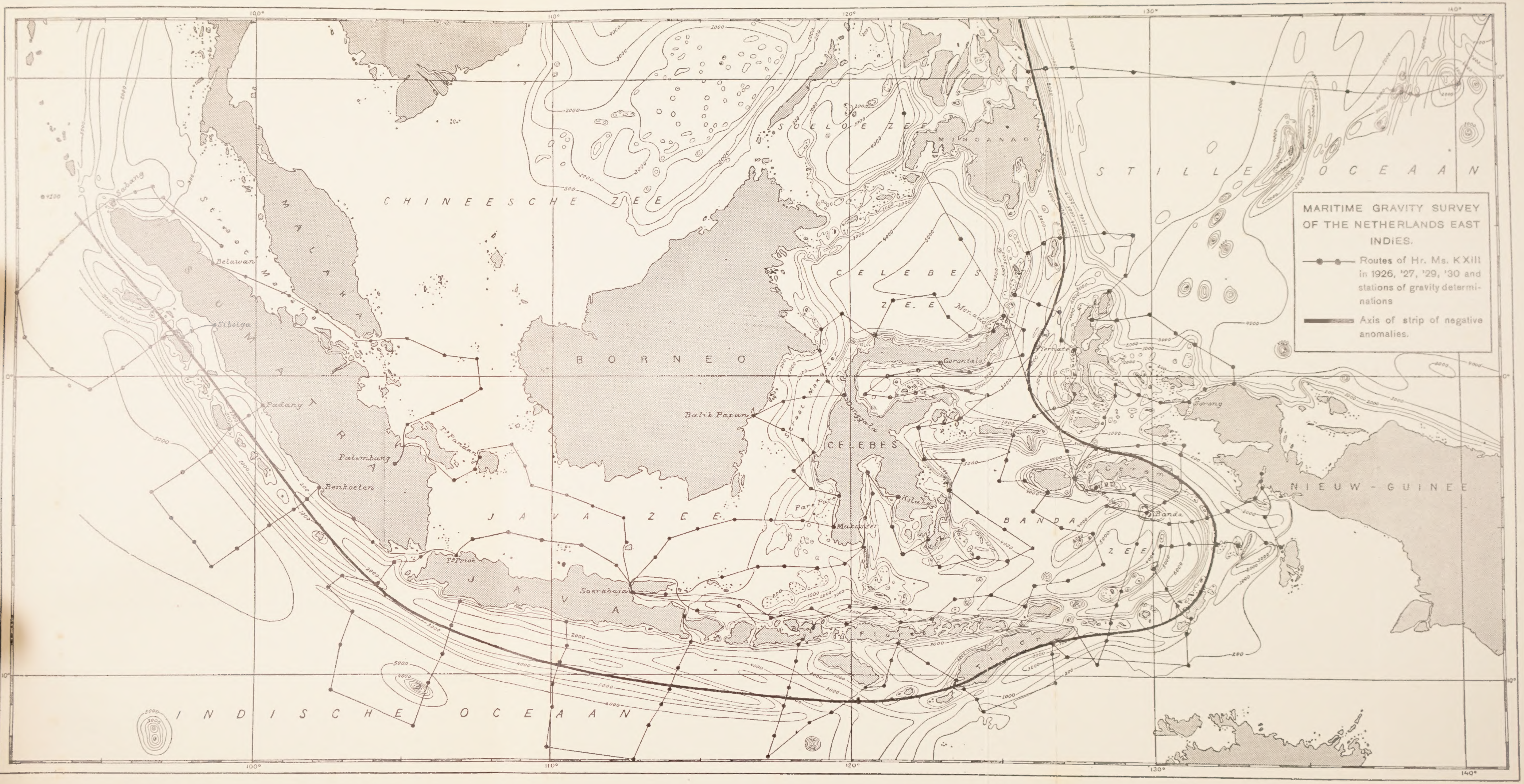
$$\frac{h d}{R}.$$

If the crust is subject to a pressure d in vertical cross-sections in every direction, the vertical force acting on the crust is double this amount pro surface unit.

If the crust is in equilibrium, this means that there must be so much more mass than the amount of mass corresponding to perfect isostasy, that the excess weight equals this vertical force. This extra layer of mass causes at the earth's surface an attraction of

$$A = \frac{3g}{2R\varrho_e} \times \frac{h d}{R} \qquad (\varrho_e = \text{mean density of the earth})$$

F. A. VENING MEINESZ: MARITIME GRAVITY SURVEY IN THE NETHERLANDS EAST INDIES; TENTATIVE INTERPRETATION OF THE PROVISIONAL RESULTS.



Proceedings Royal Acad. Amsterdam, Vol. XXXIII, 1930.

for the first case, or when introducing the values for R and for ϱ_c:

$$A = 6.7 \ 10^{-10} \ h \, d \text{ millidyne}$$

in which d is expressed in kg/cm² and h in cm.

For the second case of pressure in all directions, A is double this value.

For a crust of a thickness of 30 km. an anomaly of 40 millidynes corresponds therefore to a pressure of 20000 kg/cm² in one direction and of 10000 kg/cm² in all directions. 40 Millidynes is about the mean value of the positive anomaly which occurs in the archipelago, but possibly part of the anomaly can be accounted for otherwise as will be explained afterwards; in this case the pressure may be less.

It might be expected that the pressure in the earth's crust which has been shown to give rise to an excess of mass in the crust, would bring about a rising of the crust, but this view is not right as it neglects another consequence of the pressure, viz. the elastic compression of the crustal material [1]).

If the mean modulus of elasticity is represented by E and the mean density of the crust by ϱ_c, the excess of mass corresponding to a compressive stress d in one direction has a weight

$$\frac{h\,d}{E}\varrho_c$$

pro unit of surface. If we introduce acceptable values for E and ϱ_c, this appears to surpass the weight of the excess of mass, which the equilibrium condition requires and which is given by the formula

$$\frac{h\,d}{R}$$

The compression causes therefore an excess of weight pro surface unit

$$h\,d\left(\frac{\varrho_c}{E}-\frac{1}{R}\right).$$

If equilibrium is to be established, this must disappear by a sinking of the crust.

If ϱ_s is the density of the subcrustal layer, this sinking s is given by

$$s = \frac{h\,d}{\varrho_s}\left(\frac{\varrho_c}{E}-\frac{1}{R}\right).$$

Introducing $\varrho_c = 2.8$, $\varrho_s = 3.2$ and $E = 275000$ kg/cm² (A. PREY,

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[1]) This point has been overlooked by the writer in a former publication; the report of a lecture at the 4th Pacific Science Congress at Java, 1929.

Ueber die Elastizitätskonstante der Erde, Leipzig 1929) the sinking becomes

$$s = 2.7 \; 10^{-8} \, h \, d \qquad (s \text{ in meters, } h \text{ in cm and } d \text{ in kg/cm}^2)$$

or by taking into account the formula for the relation between anomaly and pressure

$$s = 40 \, A \qquad (s \text{ in meters, } A \text{ in millidynes}).$$

For a mean value of A of 40 md, as has been found in the archipelago, this sinking amounts to 1600 meters.

For getting an understanding of this matter a deeper study will, however, be necessary; there are several points which need further consideration. The tendency towards sinking will affect the whole region which is subject to compression and differences of E or ϱ_c will have to be taken into account. It is doubtful if the sinking will entirely keep pace with the folding process; if there is lagging this would account for part of the positive anomalies. Another part, especially near to the folding line, may be explained by the tendency towards isostatic equilibrium of the whole folding structure; the accumulation of light material may be compensated in the neigbouring parts of the crust.

So the positive anomaly corresponding to the pressure itself has possibly been overestimated and the pressure as well as the sinking may be considerably less than the computed figures.

It is hoped that a further study of this sinking tendency may explain the formation of geo-synclines and that it will enable us to account for the fact that the first stage of a mountain folding process is known to take place in a part of the earth's crust which has recently sunk below sea level. Likewise it may give an explanation of rising tendencies in a mountain system after the folding process has subsided and the compression has disappeared, in a degree which surpasses the amount resulting from re-establishment of isostasy after erosion has set in.

Although this point is not yet ripe for conclusions, it was thought well to mention it, as it suggests wariness in accepting the general belief that the results of the gravity determinations, which mostly do not deviate much from isostasy, do exclude all possibility of considerable vertical movements of those parts of the earth's crust which are not exposed to strong erosion or sedimentation. Further research and further consideration of the subject will be necessary.

Getting back to the case of the Indian Archipelago, it is clear that the origin of the compressive forces which causes the folding process, must be looked for in a South East tendency of the Asiatic continent. Australia and New Guinea do not play an active part in it but their contour line determines the shape of the corresponding part of the folding line. The strongest resistance will be exerted by the prominent parts of this contour, i.e. the curve South of East Timor and the island of Halmaheira, West of New Guinea. The abnormal high positive anomalies at the inner side of the folding line opposite to these parts, are in good agreement with the hypothesis ; North of Timor the isostatic anomaly is 120 md. and West of Halmaheira it attains even a value of more than 200 md.

Another confirmation of the theory may be found in the seismic data. which have just been published by Dr. S. W. VISSER of the Royal Magnetic and Meteorologic Observatory at Batavia in : "On the distribution of Earthquakes in the Neth. East Ind. Arch." The centres of by far the greatest number of earthquakes during the years 1920—1926 lie above or near the downward folding line. This corroborates that this is indeed the line of greatest tectonic activity in the archipelago.

The distribution of volcanoes in the archipelago shows likewise a curious correlation to the location of the folding line. Nearly all of them are situated on rows at the concave side of a curved part of this line. As the map shows, this is the case for the volcanoes of the Sangir Islands and the North Eastern arm of Celebes, for the row of volcanoes from Ternate to Batjan, West of Halmaheira, for the row of volcanoes in the inner Banda arc and for the volcanoes of the smaller Sunda Islands, Java and Sumatra. To the North and the North East of the island of Timor, where the curvature of the folding line is reversed, the inner row of islands does not show volcanoes ; this tallies as this part of the folding line is convex towards this side.

It is easy to find a plausible explanation in harmony with the above theory for the correlation of the distribution of volcanoes to the curvature of the folding line. If the earth's crust is moving from the concave side towards the folding line, the crust is stretched in a sense parallel to this line and a tensile stress develops. This might bring about fissures or at least a decrease of strength of the crust. It appears acceptable that this circumstance will favour the rising of magma and that therefore volcanoes will come into being in this part of the crust.

A contrary phenomenon might be expected to occur at the convex side of the folding line. Owing to the movement of the crust towards this line, pressure will also develop in a direction parallel to it. Perhaps the archipelago shows some instances of this compression perpendicular to the principal pressure direction. The islands Taliabu and Sula Mangoli have an East-Westerly direction, which may perhaps be ascribed to this cause. A second instance might be the great altitude of the island of Buru and a third the Siboga submarine ridge in the Banda sea, which instances occur at the convex side of the sharpest curve of this line.

If this explanation is valid, these islands ought not to show strong overthrust sheets as the shortening of the crust in a sense parallel to the folding line could not be great enough for their formation. According to the geological investigations of BROUWER on the Sula Islands, this is indeed the case on these islands.

Up to now only the principal feature of the gravity results has been dealt with. There have, however, been found other deviations but as these features are less prominent, it is premature to give details about them before the final computations and reductions are finished; the results may easily change more or less their character.

There appears to be a second line in the field of positive anomalies, where negative anomalies — much smaller than those of the principal strip — or at least smaller positive anomalies occur. This line follows the South Western arm of Celebes, runs from there towards the islands of Lombok, Bali, South of Madura and probably through Java and Sumatra. To the other side it appears to continue approximately over the Eastern arm of Celebes. Near the South Eastern arm of this island and its continuation, the Tukang Besi Islands, negative anomalies have likewise been found.

Whether the writer is right in regarding this partly as the evidence of an older folding and partly as an accompanying process of the other folding, a careful study of the final results may perhaps decide. The geology of the archipelago makes it certainly probable that formerly other foldings, to which the mountain ranges of Sumatra, Java, Borneo and Celebes correspond, have occurred nearer to the Asiatic continent. It looks as if this continent during its persistant Eastward or South Eastward tendency continually forms new folds at the outside of the older ones.

Another instance of a folding in these parts, which is now actively going on, has probably been come across during the voyage with Hr. Ms. K XIII in 1926 through the Pacific. The gravity profile found above the deeps of Guam and Yap has exactly the same character as the results above the folding line in the archipelago. The presence of the deeps and the frequency of earthquakes in those parts point in the same direction. It seems likely that those two deeps are connected with another folding line.

Mention may here be made of an abnormal low value of the anomaly found near the Asia Islands to the East of Halmaheira, which might be caused by this same folding line, because, according to the seismic data and to the topography of the ocean floor, this line appears to continue in this direction. The material is, however, too scanty to obtain certainty as to this last supposition.

If the hypothesis given in this paper about big crustal foldings is right, the ocean floors appear to have enough strength for folding processes to take place. This appears to be contradictory to the mechanism of the continental drift advocated by WEGENER. The great stresses supposed to be present in the crust likewise do not agree with this mechanism.

It is, however, another question whether the folding hypothesis is also contradictory to the principal subject of WEGENER's theory, the continental drift itself. The horizontal movement of the Asiatic continent, which this hypothesis likewise assumes to occur, renders it not improbable that both principles may be reconciled.

Between the difficult problems which will have to be solved for obtaining a satisfactory theory, one of the most difficult will be to discover the nature of the forces which are supposed to act in the crust. Besides the study of geology, volcanology, seismicity and of the topography of the sea floor, the continuation of the gravity research may be one of the means to attack this problem. Valuable knowledge would be got if the complete course of the big crustal folding lines could be determined.

For the further study of the tectonics of the Indian archipelago a gravity survey on the islands will be important; it will constitute a necessary supplement to the gravity data, which have been obtained in the past year.

Applied Geology. — *The equation of flow of oil and gas to a well after dynamic equilibrium has been established.* By J. VERSLUYS.

(Communicated at the meeting of June 28, 1930).

SYMBOLS USED IN TEXT.

p	Pressure at an arbitrary distance from the axis of the well, in atmospheres.
p_r	Pressure at the bottom of the well.
P	Pressure at which oil would be saturated with the coexisting gas.
P_1	Reservoir pressure.
a	The force exerted by atmospheric pressure per unit of area.
q	Volume of liquid flowing per unit of time through the unit of area in the cross section.
Q	Volume of liquid flowing per unit of time through the cross section which is considered.
v	Volume of gas measured at atmospheric pressure per unit of time flowing through the unit of area in the cross section.
u	Same measured at the prevailing pressure p.
R	Depletion radius.
K	Darcy's coefficient; this is the volume of a liquid which has the unit coefficient of internal friction, flowing per unit of time through the unit of area of the cross section, when the drop of pressure head is equal to the unit of force per unit of area, per unit of length.
η_0	Coefficient of internal friction (in text called viscosity) of oil.
η_g	Same for gas.
α	Absorption coefficient of gas and oil.
ϱ	Horizontal distance of the point under consideration to the axis of the well.
ε	Thickness of the oil bearing layer.
W_1, W_2, etc.	Amounts of work.

The ideal condition of the flow of oil and gas to a well is the following: The thickness of the oil bearing layer is unvaried over a great area, the layer lies nearly horizontally and the well is perforated or open opposite the whole thickness of the sand. The sand slopes at a small rate in all directions from the well to a great distance and the line of the edgewater is at a great distance from the well. The oil contains dissolved gas but pressure is at the beginning so great that the oil is not saturated with gas at this prevailing pressure; so there is no free gas before the well is opened.

Under these conditions, the motion of oil and gas may be estimated to be horizontal and so slow that kinetic energy may be neglected. So all positive work, which is performed, is counterbalanced by the work of the internal friction of liquid and gas and the former in this way is converted to heat. In the oil where work is performed by pressure differentials, some heat will be developed and this heat will tend to cause a rise of temperature. The work performed by the gas is a consequence of expansion due to which the temperature would decrease. All this work is exhausted by internal friction of the gas and consequently, in the gas the temperature would remain unaltered as long as BOYLE's law would apply and the temperature would be unaltered. Where gas is liberated from the oil, however, work will be performed which is smaller than the equivalent of the heat which is bound at its liberation. The first energy is converted to heat but this heat is not sufficient to prevent cooling caused by liberation of gas. Also, the friction in the oil does not yield sufficient heat to prevent lowering of temperature. Consequently, as a well produces oil and gas, temperature in the sand will decrease due to the liberation of gas. As soon as the edgewater approaches the well, the cooling will stop and make place for a rise of temperature due to the fact that less gas is dissolved in the edgewater than in the oil. Changes of temperature will be disregarded in the mathematical development, for sake of simplicity.

As the well is opened, pressure therein is decreased and oil and gas flow towards the well; at the same time edgewater moves towards the well. The pressure in the well, however, is so much decreased that within a certain radius R, a part of the dissolved gas is set free. Consequently, within this radius R, oil and the dissolved gas but also free gas flow to the well; outside this radius oil with only dissolved gas flow toward the well. Thus, within the radius R, depletion takes place which means that a portion of the pores of the sand no longer are filled with oil but with gas. This radius will be called the "*depletion radius*". The sand, as it has been stated before, is supposed to be not very thick and it will be presumed that the paths of the gas and the oil molecules are horizontal so that gravity exerts no work by its action on these molecules.

As it has been stated before, within the depletion radius, oil is partly displaced by gas and this oil flows to the well. This is a part of the production of the well. Consequently, the production of the well should be variable with time. If this were taken into regard, our problem would be too complicated and it will be at first supposed that a dynamic equilibrium has been established. Afterwards it can be attempted to take the influence of time into regard by means of an approximation. Because a condition of dynamic equilibrium is considered, we have assumed that the condition is independent of the time. So we assume that constant volumes of oil and gas flow per unit of time to the well. The velocity of oil and gas in the sand varies with respect to the distance to the well. According to our assumption of the case that the depletion radius does no more increase, however, pressure does not vary with respect to time. The depletion radius R is unvariable. Under these circumstances, the pressure at a distance R from the axis of the well is so great, that oil at that distance is saturated with the coexistent gas. Within this radius pressure is smaller and a part of the coexistent gas must be set free with the consequence that depletion takes place. At a distance greater than this depletion radius R from the well, pressure is so great that all coexisting gas remains dissolved. Thus, within the depletion zone, a mixture of oil and gas flows to the well while at a distance greater than this radius merely liquid with dissolved gas, which behaves as an ordinary liquid, flows to the well. Through every cylindrical surface generated by the evolution of a vertical line about the axis of the well, the same volume of oil flows to the well per unit of time and also the same amount of gas. Within the distance of the depletion radius, two conditions may occur:

first, oil and gas flow at the same speed at any distance from the well, and *second,* free gas and oil have different velocities at any distance from the well.

According as the oil approaches the well, pressure decreases and more gas is set free but at the same time gas which is already set free expands. So work is performed not only by the difference of pressures in the well and at a distance R from the well but at the same time work if performed by the gas at the moment it is set free and by its expansion (1). At the motion of oil and gas through the pores, internal friction causes resistance and this resistance performs negative work. The velocities of oil and gas, as it has been explained before, are so small that they may be neglected and practically no potential energy is converted to kinetic energy. Moreover, it has been stated that the motion will be considered to be horizontal and consequently the action of gravity on the oil performs no work.

Equations of the equilibrium will be deduced for the various quantities of work which are performed per unit of time in the space which is enclosed by the cylindrical surfaces with radii ϱ and $\varrho + d\varrho$ about the axis of the well. It will first be assumed that the first of the above mentioned conditions prevails, viz. oil and gas flow at the same speed.

Flow of an uncompressible liquid like oil is determined by DARCY's (2 and 4) law which can be written as follows:

$$q = \frac{K\alpha}{\eta_0} \frac{\partial p}{\partial x} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

if x is the distance measured in a direction opposite to the motion. The meaning of the other symbols used in this article is explained in the list at the beginning of this article.

As it has been explained in a former paper (3, page 60) for a gas this equation can be written as follows:

$$u = -\frac{K\alpha}{\eta_g} \frac{\partial p}{\partial x} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

as it has been presumed, that BOYLE's law applies to the gas. If in this equation $\frac{V}{p}$ is substituted to u, this equation is converted to:

$$v = \frac{Ka}{\eta_g} p \frac{\partial p}{\partial x} \quad \ldots\ldots\ldots \quad (3)$$

Outside the radius R, according to HENRY's law which is supposed to hold good, the amount of gas dissolved in the unit of volume of oil would occupy a volume:

$$aP \quad \ldots\ldots\ldots \quad (4)$$

at atmospheric pressure. Within this radius pressure is $p < P$, at a distance ϱ from the axis of the well and consequently at that distance a quantity of gas which occupies a volume:

$$ap \quad \ldots\ldots\ldots \quad (5)$$

at atmospheric pressure would be dissolved per unit of volume of oil. The gas which is set free per unit of volume of oil would occupy a volume:

$$a(P-p) \quad \ldots\ldots\ldots \quad (6)$$

at atmospheric pressure and:

$$a\frac{P-p}{p} \quad \ldots\ldots\ldots \quad (7)$$

at the prevailing pressure.

As long as the dynamic equilibrium, exists, a constant volume of oil Q flows per unit of time through every cylinder and this volume of oil is accompanied by a volume of gas which, according to equation (7), would occupy a volume:

$$Qa\frac{P-p}{p} \quad \ldots\ldots\ldots \quad (8)$$

at the prevailing pressure. It has been assumed that gas and oil have formed an intimate mixture. The pressure on the cylinder with radius ϱ pushes a volume of oil Q and a volume gas as expressed by formula (8) per unit of time through this cylinder. The work performed by the pressure on the oil is:

$$aQp \quad \ldots\ldots\ldots \quad (9)$$

and the work performed by the pressure on the gas is in the same way:

$$aQa(P-p) \quad \ldots\ldots\ldots \quad (10)$$

The differential of the two amounts of work performed by the pressure on the portion of the sand between the two cylinders with radii ϱ and $\varrho + d\varrho$ is the sum of the differentials of (9) and (10). So for this work may be written:

$$dW_1 = aQ(1-a)\,dp \quad \ldots\ldots\ldots \quad (11)$$

Within the space between the two cylinders we considered, part of the gas is dissolved and a part of the gas is free. As it enters this space, gas and liquid have a pressure $p + dp$ and as they leave this space the pressure is p. In a former paper (1), it has been proved that the amount of work performed does not change in case a part of the gas is dissolved in liquid and saturates same. This has been deduced as follows: If the considered liquid is saturated at a pressure $p + dp$ with an amount of gas which at atmospheric pressure occupies volume V_1, and if the amount of gas which is free would occupy the atmospheric pressure volume V_2, the increment of volume of the free gas is: $\frac{V_2}{p} - \frac{V_2}{p + dp} = V_2 \frac{dp}{p}$ according as pressure decreases to p. At a pressure p the volume of this amount of gas would have been $\frac{V_2}{p} dp$. The volume of the dissolved gas which would have been V_1 at a pressure $p + dp$ would have been reduced to a volume $V_1 \frac{p}{p+dp}$ as pressure would have decreased to p, both volumes measured at atmospheric pressure. So as the pressure decreases from $p + dp$ to p an amount of gas is set free, the volume of which would be $V_1 — V_1 \frac{p}{p+dp} = \frac{V_1}{p} dp$ and at the prevailing pressure the volume would be $\frac{V_1}{p^2} dp$. As a consequence of the decrease of pressure, the volume of liquid and the coexistent gas has increased $(V_1 + V_2) \frac{dp}{p^2}$. The work performed at this increase of volume is $(V_1 + V_2) \frac{dp}{p}$. So the work performed is independent of the presence of liquid in which a part of the gas is dissolved at the prevailing pressures, as the sum $V_1 + V_2$ is not changed by the presence of the liquid. So the work performed at the liberation and the expansion of gas within the space we considered is:

$$dW_2 = a\,\alpha P Q p \left(\frac{1}{p + dp} - \frac{1}{p}\right) = a\,\alpha P Q \frac{dp}{p} \quad . \; . \; . \quad (12)$$

The work which is performed per unit of time by the friction resistance in the space we considered can be expressed as follows: The total volume which flows per unit of time through the inner cylinder is the sum of the volumes of oil and gas expressed by (8):

$$Q + Q\alpha \frac{P - p}{p} = Q \frac{p + \alpha P - \alpha p}{p} \quad . \; . \; . \; . \; . \quad (13)$$

Per unit of area, this volume is:

$$\frac{Q}{2\,\pi\varrho\varepsilon} \frac{p + \alpha P - \alpha p}{p} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

In case q units of volume of oil would flow through the unit of area in the cross section and no gas, the resistance in this space would be:

$$-\frac{q\eta_0}{K}\,d\varrho \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

and the total force exerted by this resistance would be:

$$-2\,\pi\varrho\varepsilon\,\frac{q\eta_0}{K}\,d\varrho \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

This force would exert an energy per unit of time:

$$-2\,\pi\varrho\varepsilon\,\frac{q^2\eta_0}{K}\,d\varrho \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (17)$$

If instead of q the value of formula (14) is substituted, formula (17) is converted to:

$$-\frac{Q^2}{2\,\pi\varrho\varepsilon}\,\frac{\eta_0}{K}\left\{\frac{p+\alpha P-\alpha p}{p}\right\}^2 d\varrho \quad . \; . \; . \; . \; . \; . \; . \quad (18)$$

In the same way for the work of resistance in the gas the following equation can be deduced:

$$-\frac{Q^2}{2\,\pi\varrho\varepsilon}\,\frac{\eta_g}{K}\left\{\frac{p+\alpha P-\alpha p}{p}\right\}^2 d\varrho \quad . \; . \; . \; . \; . \; . \; . \quad (19)$$

The volume in which the pores are filled with oil in the solid we considered is expressed by:

$$2\,\pi\varrho\,d\varrho\,\frac{p}{p+\alpha P-\alpha p} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

and the volume in which the pores are filled with gas is:

$$2\,\pi\varrho\,d\varrho\,\frac{\alpha\,(P-p)}{p+\alpha P-\alpha p} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (21)$$

So the total work performed per unit of time by friction resistance in the solid we considered is:

$$dW_3 = -\frac{Q^2}{2\pi K\varepsilon}\,\frac{(p+\alpha P-\alpha p)\,(\eta_0\,p+\eta_g\,\alpha P-\eta_g\,\alpha p)}{p^2}\,\frac{d\varrho}{\varrho} \quad . \quad (22)$$

The algebraic sum of the various amounts of work must be O, hence, we may write:

$$dW_1 + dW_2 + dW_3 = 0, \quad . \; . \; . \; . \; . \; . \; . \quad (23)$$

or:

$$\left.\begin{array}{c} \alpha Q\,(1-\alpha)\,dp + \alpha\,\alpha PQ\,\dfrac{dp}{p} - \\ -\dfrac{Q^2}{2\pi\varepsilon K}\,\dfrac{(p+\alpha P-\alpha p)\,(\eta_0\,p+\eta_g\,\alpha P-\eta_y\,\alpha p)}{p^2}\,\dfrac{d\varrho}{\varrho} = 0 \end{array}\right\} \quad . \quad (24)$$

The variables can be separated as follows:

$$\frac{Q}{2\pi\varepsilon K a}\frac{d\varrho}{\varrho}=\frac{p\,dp}{\eta_0\,p-\eta_g\,\alpha p+\eta_g\,\alpha P} \quad \ldots\ldots \quad (25)$$

The second of the above mentioned conditions: oil and gas flow at different velocities will also be considered. In order to solve this problem, two equations of equilibrium will be deduced, one for the work performed in the oil and one for the work performed in the gas. It will be presumed that in the cylindrical surface about the axis of the well with the radius ϱ which has an area $2\pi\varepsilon\varrho$ within the sand in a portion $2\pi\varrho y$ the pores are filled with oil and in a portion $2\pi\varrho\ (\varepsilon-y)$ with gas. For a dynamic equilibrium, it is necessary that at the same distance ϱ pressure in oil and gas are the same. The pressure differential caused by the height of the column of liquid will be neglected as it has been done before.

The work performed by pressure is:

$$dW_1=aQ\,dp \quad \ldots\ldots\ldots \quad (26)$$

and the work of the resistance:

$$dW_3=-\frac{Q^2\,\eta_0}{2\,\pi\varrho\,yK}\,d\varrho \quad \ldots\ldots\ldots \quad (27)$$

The equilibrium is expressed by:

$$dW_1+dW_3=0 \quad \ldots\ldots\ldots \quad (28)$$

or:

$$aQ\,dp-\frac{Q^2\,\eta_0}{2\,\pi\varrho\,yK}\,d\varrho=0 \quad \ldots\ldots\ldots \quad (29)$$

This equation can be transformed as follows:

$$2\pi\,Ka\,y\,dp=Q\,\eta_0\,\frac{d\varrho}{\varrho} \quad \ldots\ldots\ldots \quad (30)$$

This is the equation of the equilibrium of the work per unit of time performed in the oil. For the gas the following deduction can be made.

The work of pressure is:

$$dW_1=-\,a\,\alpha Q\,dp \quad \ldots\ldots\ldots \quad (31)$$

The work performed by the gas at its liberation and its expansion is again expressed by equation (12). The work of the resistance is expressed by equation (28), if we substitute $\varepsilon-y$ for y, η_g for η_0 and if Q is replaced by the volume of the free gas at the pressure ϱ. This gas volume is expressed by equation (7). So we may write:

$$dW_3=-\left(\frac{P-p}{p}\right)^2 Q^2\,\frac{\eta_g\,\alpha^2}{2\,\pi\varrho\,(\varepsilon-y)\,K}\,d\varrho \quad \ldots\ldots \quad (32)$$

An equation of equilibrium can be deduced from the equations (32), (12) and (33):

$$dW_1 + dW_2 + dW_3 = 0 \quad . \; . \; . \; . \; . \; . \; . \quad (33)$$

or:

$$-\, a\,\alpha Q\,dp + a\,\alpha PQ\frac{dp}{p} - \left(\frac{P-p}{p}\right)^2 \frac{Q^2\,\eta_g\,\alpha^2}{2\,\pi\,K\,(\varepsilon - y)}\,\frac{d\varrho}{\varrho} = 0 \quad . \quad (34)$$

or:

$$2\,\pi\,Ka\,(\varepsilon - y)\,dp = Q\,\eta_q\,\alpha\,\frac{P-p}{p}\,\frac{d\varrho}{\varrho} \quad . \; . \; . \; . \; . \; . \quad (35)$$

This is the equation of the equilibrium of gas which combined with the equation (30) for oil will yield the solution of the problem. The equations (30) and (35) are two simultaneous differential equations in which the three variables ϱ, p and y enter and the differentials of ϱ and p. From these two differential equations y may be eliminated and again equation (25) is obtained:

If we integrate this equation between two arbitrary limits of each variable, respectively, ϱ and ϱ_1, p and p_1, this equation gives the following solution:

$$\frac{2\,\pi\,Ka\varepsilon}{(\eta_0 - \eta_g\,\alpha)^2 Q}\left[(\eta_0 - \eta_g\,\alpha)\,(p - p_1) - \eta_g\,\alpha P \lg \frac{(\eta_0 - \eta_q\,\alpha)\,p + \eta_g\,\alpha P}{(\eta_0 - \eta_g\,\alpha)\,p_1 + \eta_g\,\alpha P}\right] = \lg\frac{\varrho}{\varrho_1} \quad (36)$$

If equation (25) is integrated between the limits r and R, respectively, p_r and P, the following equation is obtained:

$$\left.\begin{aligned} &\frac{Q}{2\,\pi\varepsilon\,Ka}\lg\frac{R}{r} = \\ &= \frac{1}{(\eta_0 - \eta_g\,\alpha)^2}\left\{(\eta_0 - \eta_g\,\alpha)\,(P - p_r) - \eta_g\,\alpha P \lg \frac{\eta_0\,P}{(\eta_0 - \eta_g\,\alpha)\,p_r + \eta_g\,\alpha P}\right\} \end{aligned}\right\} \quad (37)$$

It has been presumed in the foregoing deductions that η_0 is independent of the pressure. This is not exact, but as now no data concerning the variation of the viscosity of oil with the amount of gas dissolved are known.

Another point has been neglected in the above formulae. The volume of the liquid also depends on the amount of gas dissolved in the oil. For the moment no data re this question are available.

Furthermore it has been accepted that a dynamic equilibrium has been established.

If in the above formulae (25, 36 and 37) we substitute $\alpha = 0$ which means that gas is insoluble, we obtain:

$$\frac{Q}{2\,\pi\varepsilon\,Ka}\,\frac{d\varrho}{\varrho} = \eta_0\,dp, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (38)$$

$$Q = \frac{2\,\pi\,Ka\,\varepsilon}{\eta_0}\,\frac{p - p_1}{\lg\varrho - \lg\varrho_1} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (39)$$

and

$$Q = \frac{2\,\pi\,Ka\,\varepsilon}{\eta_0}\,\frac{P - p_r}{\lg R - \lg r} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (40)$$

Supposing that gas is insoluble, means that no gas is present, and the pores are wholly filled with oil. There would not be a material depletion. Formula (40) is practically J. DUPUIT's (5 and 6) formula for the flow of water to an artesian well.

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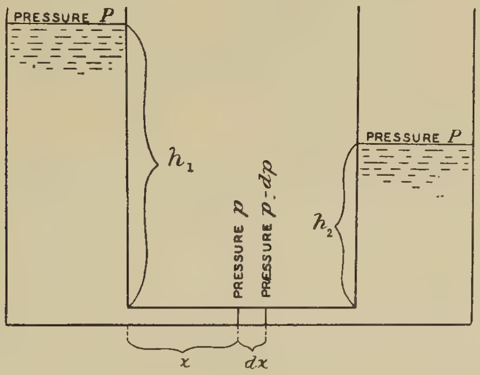
Hydraulics. — *Motion of gasbubbles in a horizontal flow of liquid.*

By J. VERSLUYS.

(Communicated at the meeting of June 28, 1930)

In case a liquid moves horizontally and there is a certain resistance, there must be differentials of pressure in order to maintain the motion, and due to these differentials of pressure, a gas bubble in the liquid will tend to move in the same direction as the liquid but at a greater speed.



Suppose two reservoirs, as shown in the accompanying figure, are connected at the bottom by means of a horizontal tube. These reservoirs are filled with liquid to different levels and consequently the liquid will flow through the tube from one reservoir to the other. It will be accepted that the water levels in the reservoir do not change and that kinetic energy of the water may be neglected. There is turbulence in the tube and this causes resistance. According to this, there must be a drop of pressure head in the tube between the two reservoirs. We take dp for the drop of pressure on the interval of length dx. A gas bubble which would have a volume v_0 at the pressure p_0 moves a distance dx to the right, the direction in which the pressure head decreases. At this displacement, the volume of the bubble increases from

$$\frac{p_0 v_0}{p} \text{ to } \frac{p_0 v_0}{p-dp}.$$

So the increment of volume is:

$$\frac{p_0 v_0}{p^2} dp \quad \ldots\ldots\ldots\ldots \quad (1)$$

The gas in the bubble has expanded and owing to this it has performed a work:

$$\frac{p_0 v_0}{p} dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

At the same time a volume of liquid $\frac{p_0 v_0}{p^2} dp$ is lifted to the surface. If at first we do not venture any speculations about the reservoir in which this liquid rises but suppose that this volume of liquid is lifted to a height h, then gravity performs a work:

$$-\gamma_l \frac{p_0 v_0}{p^2} h\, dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

if the specific weight of the liquid is γ_l. Besides, the liquid raises the surface of one of the reservoirs or of both reservoirs on which the atmosphere exerts a pressure P, and consequently the pressure of the atmosphere exerts a work:

$$-\frac{p_0 v_0}{p^2} P\, dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

So regardless of the entraining action of the motion of liquid on the bubble, this will tend to move to the right in case:

$$\frac{p_0 v_0}{p} dp > \gamma_l \frac{p_0 v_0}{p^2} h\, dp + \frac{p_0 v_0}{p^2} P\, dp \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or if:

$$p > \gamma_l h + P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If we presume $h = h_2$, this formula is converted to:

$$p > \gamma_l h_2 + P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The right member of this formula represents the pressure at the right end of the tube and the pressure p is greater than this pressure so that this formula is accomplished. Consequently, the free gas will tend to move horizontally at a greater speed then the surrounding liquid.

This phenomenon, the tendency of gas to migrate horizontally faster than a surrounding liquid is of some importance for the study of flow of gas and liquid in a porous medium.

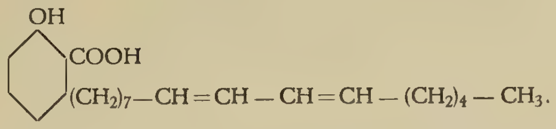
The difference of speed between gas and liquid in a vertical channel has been dealt with by the author in former papers, especially in "The cause of periodicity generally occurring with rising mixtures of gas and liquids" presented to the Academy in the May meeting, and in the papers mentioned at the foot of that paper.

Chemistry. — *Minjak Pelandjau, the exudation from the wood of Pentaspadon Motleyi Hook f.* By P. VAN ROMBURGH, A. G. VAN VEEN and A. J. HAAGEN SMIT. (Second communication).

(Communicated at the meeting of May 31, 1930).

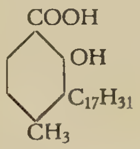
In a provisional communication on this subject, published about a year ago[1], we showed that pelandjauic acid must possess five ethenoid linkages, one hydroxyl group and a ring-system.

Three months later JONES and SMITH[2] published the results of their investigation of the same acid, to which they gave the name of pentaspadonic acid. Those results led them to suggest the following structure for the acid:



They emphasise however, that no finality is claimed for this structure.

Our investigation of the acid has been continued and has led us to a conclusion which differs in several points from that of JONES and SMITH. When all the facts recorded in the present paper are fitted together they constitute a very probable proof that the structure of this acid may be represented as follows:



Tetrahydro-pelandjauic acid $C_{25}H_{42}O_3$.

This acid was prepared by saponifying the methyl ester, described in our provisional paper, with alcoholic potassium hydroxide during eight hours.

The pure acid, recrystallised from petroleum ether and methanol, forms colourless crystals, melting at 93—94°. It gives a violet colouration with alcoholic ferric chloride. JONES and SMITH, who obtained this acid as a by-product from the Zeisel determination of methoxyl in the crystalline ether-ester, found for the melting point 88°.

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[1] This Proceedings Vol. **32**, 693 (1929).

[2] Proc. Royal Soc. of Queensland XLI N°. 6, 73 (1929).

Analysis: Found: C 76.66, 76.11, 76.63, 76.79, 76.71.
H 11.96, 11.05, 10.96, 10.87, 11.03.
$C_{25}H_{42}O_3$ requires: C 76.85; H 10.85.
$C_{24}H_{40}O_3$ „ C 76.54; H 10.71.

The difficulty of deciding between those formulae would be solved by the determination of the molecular weight of the acid by titration.

Found: 387, 381, 387, 387, Mean 388.
$C_{25}H_{42}O_3$ requires 390.
$C_{24}H_{40}O_3$ „ 376.

Methyl tetrahydro- and decahydro-pelandjauate methyl ether.

The methyl ether-ester of pelandjauic acid was prepared by the method given by Jones and Smith (loc. cit.). From 5 grams of the acid we obtained 4 grams of the ether-ester as a liquid boiling at 223—225° (0.4 mm).

Methoxyl determination: Found: OCH_3 14.06
$C_{24}H_{36}OCH_3 . COOCH_3$ requires: OCH_3 14.98
$d_4^{15} = 0.9697$, $n_D^{15\ 2} = 1.5067$.

Hydrogenation of this ether-ester with platinum black in ethyl acetate produced, according to Jones and Smith, the tetrahydroderivative which, crystallised from alcohol, melted at 45—46°.

Hydrogenation with platinum oxide gave a decahydroproduct melting at 49—51°.

Analysis: Found: C 76.87, 76.92; H 12.56, 12.52.
$C_{27}H_{52}O_3$ requires: C 76.4; H 12.3.

Oxidation of the tetrahydro-ether-ester.

1 gram oxidised with CrO_3 in acetic acid yielded a crystalline acid, the sodium salt of which was recrystallised from alcohol. The acid was liberated with hydrochloric acid and recrystallised from petroleum ether and from alcohol. It melted at 67—68° and proved to be *stearic* acid. Melting point of the anilide 93°. Both products were identified by a mixed melting point determination.

Decarboxylation of pelandjauic acid.

In our provisional communication we showed that by heating pelandjauic acid only carbon dioxide is evolved. With a purified acid, heated in a current of nitrogen at 200—220°, the amount of CO_2 corresponds with 1 mol.

The liquid product, formed in this process, boiled at 210—215° (0.5 mm.). It contains one OH-group as was determined by the method of ZEREWITINOFF.

Found: 5.61 % OH

$C_{24}H_{38}O$ requires: 4.97 %.

This phenol did not give a reaction with ferric chloride. It is insoluble in sodium hydroxide solution.

Hydrogenation of the phenol $C_{24}H_{37}OH$.

1 gram was hydrogenated with platinum black in ethyl acetate. The purity of this product being very high, it was found that quickly 5 mol of hydrogen were taken up.

The decahydroproduct, recrystallised from ethyl acetate and methanol, melted at 35°.

Hydroxyl determination: Found: OH 5.26.

$C_{24}H_{37}OH$ requires: 5.04.

In another experiment a substance was obtained, which did not contain oxygen. The hydrocarbon formed in this reaction, recrystallised from alcohol and ether, melted at 34°.

Analysis: Found: C 85.56; 85.48, 85.67.

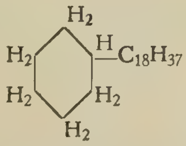
H 14.55, 14.24, 14.24.

$C_{24}H_{48}$ requires: C 85.67; H 14.39.

M. W. determination in camphor by RAST's method. Found: 341; $C_{24}H_{48}$ requires: 336.

The hydrocarbon $C_{24}H_{48}$, the formula of which is in agreement with the analytical results from the experiments on tetrahydro-pelandjauic acid recorded in the present paper, must contain a ring with a side-chain of 17 or 18 C-atoms. This indicates in the tetrahydroderivatives the presence either of a benzene nucleus or a system of an open chain of conjugated unsaturated linkages.

The difficulty with which the hydrogenation proceeds in the tetrahydroproducts is in agreement with the hypothesis of a benzene nucleus. An hydrocarbon $C_{24}H_{48}$ containing a hydrogenated benzene nucleus and one side-chain must be represented by the formula of an octadecylcyclohexane $C_6H_{11} . C_{18}H_{37}$.



We prepared this hydrocarbon by the interaction of magnesium on a mixture of cyclohexanebromide and stearylbromide in benzene solution.

The melting point is 35°. Both hydrocarbons were found to be *not* identical, the melting point being depressed 4° on admixture.

These results suggest that the nucleus may contain two side-chains.

Methylation of the phenol $C_{24}H_{37}OH$ formed by decarboxylation of pelandjauic acid.

The methyl ether was prepared by shaking the phenol with dimethyl sulfate and sodium hydroxide solution. It boiled at 200—205° (0.2 mm). The determination of the methoxyl group gave a negative result, proving that this ether is remarkably resistent to the action of concentrated hydroiodic acid.

$$n_D^{15} = 1.5052; \qquad d_4^{15} = 0.9146.$$

Found: M_D 115,6

$C_{25}H_{40}O\ |\overline{\overline{5}}$ requires: M_D 114,6.

Hydrogenation of the methyl ether of the phenol.

By hydrogenation in ethyl acetate with platinum black two molecules of hydrogen were quickly absorbed. The tetrahydroproduct after recrystallisation from ethyl acetate and methanol separated in plates, melting at 38°.

Analysis: Found: C 83.21, 83.06; H 12.41, 12.53.

$C_{25}H_{44}O$ requires: C 83.33; H 12.31.

The determination of the methyl group gave no results.

On further hydrogenation with platinum oxide in ethyl acetate, 3 mol hydrogen were taken up. In this decahydroderivative, melting at ± 25°, the determination of the methoxyl group by ZEISEL's method succeeded better and gave the following results:

Found: OCH_3 6.1, 5.8.

$C_{24}H_{47}OCH_3$ requires: OCH_3 8.4.

Oxidation of the methyl ether of the tetrahydrophenol.

Potassium permanganate has no action; after heating with the calculated quantity during 48 hours the ether was obtained unchanged. Oxidation by heating the ether with a 10 % solution of chromic acid in acetic acid gave stearic acid, which was identified in the same manner as in the case of the tetrahydroether-ester of pelandjauic acid.

Dehydration of the decahydrophenol.

In order to split off water, this product was heated with $ZnCl_2$ at 180—190°. The reaction mass was poured into water and an hydrocarbon separated. It boiled at 175—180° (0.3 mm.) and melted at 25°:

$$d_4^{19} = 0.838 \qquad n_D = 1.4664.$$

M_D Found: 110,5

$C_{24}H_{46}$ requires 110,4,

Ozonisation of the hydrocarbon $C_{24}H_{46}$.

The hydrocarbon was ozonised in a 10 % solution in tetrachloromethane during twelve hours. From 4 g. hydrocarbon were obtained 1.8 gr. acid, soluble in sodium hydroxyde solution, 0.3 g. acid insoluble and 0.1 g. neutral products, which were not examined. The determination of the mol. weight of the first acid and that of the silver content in the silver salt showed results in disagreement with those required for a pure product.

Therefore the silver salt was converted into the methyl ester, which boiled at 220—222° (0.3 mm.). Colourless crystals melting at 48—50°.

Analysis: Found: C 75,26; H 12,27.

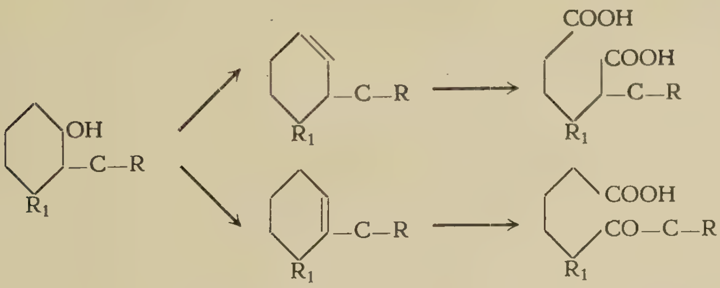
$C_{24}H_{48}O_3$ requires: C 75,75; H 12,71.

Methoxyl determination: Found: OCH_3 7,4.

$C_{24}H_{48}O_3$ requires: OCH_3 7,8.

These results suggest that this acid contains one keto- and one carboxyl group.

The methoxyl determination in the non-crystalline part of the ester gave 9.50 % OCH_3. This result pointed to the fact of this product being a mixture of esters of a keto- and a dicarboxylic acid.



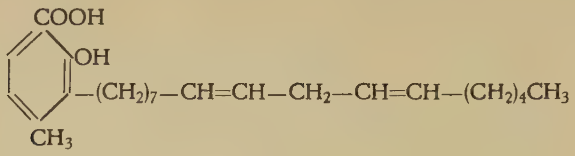
From the results obtained in this investigation the conclusion may be drawn that the formula of pelandjauic acid is:

$$C_6H_2COOH \,.\, OH \,.\, R_0 \,.\, R_1.$$

The side-chain R_0 must contain two double linkages.

(Postscript of July 10th. It will be shown in a later article that several facts establish beyond doubt R_1 to be a CH_3 group.)

The full structure formula of the acid is as follows:



In the fruits of a plant belonging to the same family viz. Anacardium occidentale L. occurs an acid, (STÄDELER, Annalen **63**, 154 (1847), RUHEMANN and SKINNER, Ber. **20**, 1861 (1887)), named anacardic acid, bearing a striking resemblance to the acid from Pentaspadon Motleyi.

In the wood of trees belonging to the genus Rhus occur substances containing also long normal side-chains.

Utrecht, Organic-chemical Laboratory
of the University.

Psychology. — *Comparison of a few intellect-tests.* By Dr. D. WIERSMA. (Communication from the Laboratory of the State Asylum for Psychopaths, Leyden.) (Communicated by Prof. E. D. WIERSMA.)

(Communicated at the meeting of June 28, 1930).

The experimental investigation of the intellect may be set about in two ways, which differ from each other in principle. In the first place we can apply a method which gives us an insight into the intellectual performances of the test-person as a whole, which enables us to determine whether there is a debility or dementia, or on the other hand a more than normal endowment. What the nature of the defect is, in what direction a special talent lies, cannot, however, be determined with the aid of methods of this kind. The level of intelligence, determined by the BINET-SIMON method, tells us how far a child is in general ahead of or behind his age, but it does not give any clue as to the causes of the differences found. And the results obtained with tests like those of the American army inquiry, although well-suited for the very accurate demonstration of differences in intellectual development and endowment both within and without the normal limits, are restricted to a measure of the intelligence in general; they teach us nothing as to the separate elements which combine to form so complicated a function as the intellect. The importance of these general methods lies first and foremost in their practical application. For ascertaining whether a child should be at a school for mentally defective children, or in a class for specially gifted ones, the BINET-SIMON method is a greatly to be appreciated aid, and the brilliant results which psycho-technics have obtained with the American army inquiry and with allied series of tests, not only in the organisation of the army itself, but also in industry, hardly need to be recalled. In pathology, also, such level-methods can most certainly be applied with good results, as is clearly shown by the value which a test according to the BINET-SIMON method has for the diagnosis of debility or of dementia. Yet the determination of the level of intelligence in the case of adults is found to be nothing like so reliable as with children; it not infrequently occurs that there is a very great difference between the age-level at which all the tests still yield positive results, and that at which all the results have become negative. The calculation usually applied, according to which every properly answered question of an age level of which not all the tests can be calculated positively, counts for $^1/_5$ of a year, begins therefore to lose much of its value. I found, for instance, in the case of a patient of the age of 44, who was admitted into the Psychopathic Asylum, that all the questions for the age of 5 were properly answered, of those for 6 years he answered 4 properly, of those for 7 years 3, of those for 8 years 2, for 9, 10, and 12 years each 1, whilst the tests for the age of 15 years were the first to yield nothing but negative results. According to the usual calculation we should therefore get an intelligence level corresponding to $5 + {}^{12}/_{5} = 7{}^{2}/_{5}$ years, but it need hardly be said that a result of this kind has little more than a conventional value. The question now is, to what such unsatisfactory results, which repeatedly occur in the case of adult test-persons, are to be ascribed. And then we have to remember that Binet and Simon especially chose their tests so that as far as possible every kind of intellectual performances could be tested thereby: the repetition of dictated figures, counting backwards from 20 to 1, the giving of definitions, the criticizing of absurd sentences and of pictures with defects, the construction of sentences with three given words, are tests which have regard to very different sides of the intellect. And if a defective development or an acquired defect does not manifest itself on all these sides uniformly, then such discrepant results of the test are to be anticipated; the negative results have then to be obtained chiefly with similar tests. In the case of the patient mentioned it was more especially the tests which called for judgment and criticism in which he failed, such as the description of pictures, which usually give positive results at the age of 7, and the pointing-out of the difference between allied ideas and of defects in pictures belonging to the age of 8, whilst tests in which observation was an important factor: the arrangement of weights, which should be positive at the age of 10, and the offering of resistance to suggestion, when three pairs of lines are first shown, of which the right one is the longer, but afterwards three pairs which are of equal length, which should only be performed successfully at the age of 12, gave in his case positive results.

It must therefore be of importance to be able to test the separate functions also, which together form the parts of the intellect. And in this consists the second procedure which may be applied in the experimental investigation of the intellect, and which has the advantage of enabling us to determine which functions in the case of a feeble-minded or demented patient are chiefly deranged, in what direction an individual above the average is specially gifted. By testing each of the various elements of the intellect individually, and then combining the results obtained with one another, we are able by applying this method, just as well as by employing the first one, to form an idea of the intellect as a whole. But we can furthermore take into account the results of our tests for the measures to be taken in each case, which will be of especial importance if we wish to indicate the direction in which gifted young people can pre-eminently develop. Still greater is the theoretical importance of such an investigation. In the first place it is calculated to enable us to distinguish various forms of dementia from one another, since it gives an answer to the question whether in different forms the principal disturbance is not to be found in different functions. But besides this it is the only way in which we can ascertain whether and to what extent particular elementary functions co-operate to produce intellectual performances. For this purpose it is not sufficient to devise a number of very heterogeneous tests; each of these must satisfy three demands:

1⁰. The activity demanded of the test-person must resemble that which we have per definitionem attached to a particular function.

2⁰. There must be a high degree of consistency between the results of tests which are directed to one and the same function.

3⁰. The consistency between the results of tests by means of which various functions are tested, must only be very slight; only in this case is a sharp distinction between the various elements of the intellect possible.

It is impossible within the scope of this paper to enter into the question whether it is justified and appropriate to reckon functions like the memory and the power of association to the elements of the intellect. Opinions differ on this point; the differences in opinion are partly due to a question of the interpretation of words, but they are also partly a question of principle. To decide on and defend a point of view would necessitate highly detailed expositions, which would here be out of place. I will therefore confine myself to discussing tests in connection with two functions, which are universally admitted to belong to the intellect: the *judgment* and the *imagination*.

For testing the judgment all kinds of different tests are in use. Miss BRUGSMA (3) made use of the definition method, ALBERTIJN (1), and ARKEMA (2) worked with pictures in which absurdities had to be pointed out. This latter method especially, which is easy of application, usually arouses the interest of the test-person to a high degree, and yields results which are pretty well independent of the subjective judgment of the tester, must be regarded as pre-eminently suited for the investigation of the judgment. ARKEMA easily found a number of absurd pictures, which, in accordance with BOBERTAG's requirements were correctly judged by 70 % of his normal test-persons of the working-class. At the psychopathic asylum, in addition to other tests in the same category, a series of 6 pictures is regularly used, in which the patients are required to point out the absurdity. This series consists of 1⁰. a cart drawn by three men, whilst a horse holds the reins, 2⁰. a fish in a birdcage, 3⁰. a hunter trying to catch a hare with his hands, although he has a gun over his shoulder, 4⁰. a clock with the long hand pointing to 12, but the small one between 1 and 2, 5°. a few trees lit up by the setting sun, one of which throws its shadow towards the sun, and 6⁰. a burning candle which throws a shadow of itself. It is found that the three last pictures are much harder to judge than the first two. Altogether they give results which agree very well with the other judgment tests. I have used them as material for comparison with the investigation to be discussed here.

For testing the imagination, also, various methods are in use. Prof.

WIERSMA (6), SCHULTE (5), and later ARKEMA (2) have made use of these methods with normal persons and with sufferers from various psychoses, and have found that they are very suitable for use as a method of testing the intellect. As is well-known, one procedure consists in showing the test-person each time a series of pictures in which the same object is represented in various degrees of distinctness, by focussing the camera with which they were photographed more or less sharply. The least distinct pictures are shown first, then follow pictures which gradually become clearer, in such a way that each series comprises six pictures. Note is taken of the number of pictures properly recognized by the test-person. With the other method the Dutch word "droom" (dream) is used, a note being made of the number of words with a meaning which the test-person, by omitting and transposing letters, can make in three minutes. The maximum number of words is 12, viz. moord (murder), oord (place), moor (moor), room (cream), oom (uncle), door (through), rood (red), oor (ear), drom (troop), dom (stupid), om (around), dor (arid), or 14, if such unusual words as do (musical note) and mor (present tense of the verb "morren" — to grudge) are counted, but normal test-persons of the working-class hardly ever reach this maximum; Professor WIERSMA found that they may be counted on to find 5 or 6 words. With medical students this number is, however, considerably higher; I found that amongst them the maximum was not infrequently attained. This difference must be attributed partly to selection, partly to better development of the function in question by practice.

Of late Professor WIERSMA has indicated still another method, which might serve as parallel test to the hazy photographs, by applying the principle of sensations constantly increasing in distinctness to the sense of touch instead of to that of sight. Generally known objects are wrapped for this purpose in flannel, in such a manner that the first object is surrounded by six layers, the second of the same sort by 5, the 3rd by 4, the 4th by 3, the 5th by 2, and the 6th only by one layer of flannel. The test person is given the packages in this order to feel with the 2nd and 3rd fingers of the right hand, and note is then taken of the number of objects that he can recognize properly. The checking of this test is the most important part of this investigation. What we had to do was to determine whether this test was really a test of the imagination, and whether there was a sufficient connection with the intellectual performances in general. With this object, after having experimented with 25 patients admitted to the psychopathic asylum, I calculated the correlation between the results of the test of the wrapped-up objects on the one hand and that of the hazy photographs, the words from "droom", and the absurd pictures each separately on the other hand. In order, however, to be sure that the three latter tests are really good comparative material, I also calculated their reciprocal correlations.

For although SCHULTE and ARKEMA had demonstrated the existence of a connection between the results of the photographs test, the "droom" test, and the general intellect-tests, they employed for this purpose the so-called four-fields method. And although this is capable of showing an existing connection, it does not lend itself to a quantitive correlation calculation. I therefore prefer the formula of BRAVAIS-PEARSON. Since KAPTEIJN (4) showed that the fraction obtained by means of this formula is a measure of the relation between the number of common factors which have contributed to the results of two tests and the total number of factors which have been of influence, we know that in this correlation we possess a very accurate measure of the connection between the performances found. If all the factors which in the one test lead to a favourable result, do so in the other test also, and all counteracting influences likewise work in the same direction in both tests, without there being causes which make their activity felt in one test only, then the correlation between the two is + 1, which of course in actual practice no more occurs than does the converse case, in which all the factors which bring about a favourable result in the one case, lead to an unfavourable result in the other, so that the correlation would be equivalent to — 1. If the two tests are quite independent of each other, then the correlation is 0. If two tests are to serve for the investigation of the same function, then they must display a not too slight positive mutual correlation ; this is usually required to amount to + 0.4 to + 0.5.

The tests with the wrapped-up objects were carried out with 25 test-persons, all patients of the psychopathic asylum. There were 7 series of 6 packages to be felt, in which were hidden : 1⁰. a matchbox, 2⁰. a key, 3⁰. a bottle, 4⁰. a button, 5⁰. a pair of scissors, 6⁰. a spoon, and 7⁰. a wire nail. The number of properly recognised objects amounted per test-person to an average of 28.5, distributed as follows over the various objects :

TABLE I.

Object	Properly recognized	Average per t.p.
Matchbox	135	5.4
Key	118	4.7
Bottle	112	4.5
Button	93	3.7
Scissors	88	3.5
Spoon	85	3.4
Wire-nail	82	3.3
Total	713	28.5

This result shows that the matchbox was the easiest to recognize, the wire-nail the hardest, and that the various objects in the above order —

which was purposely not adhered to during the tests with the various test-persons, but constantly changed — increased in difficulty. At the same time it also leads to the supposition that the test with the matchbox, in which more than 5 out of 6 packages were properly identified, is somewhat too easy for our purpose. This is shown still more clearly by the checking by the number of objects which should be recognized in each group by normal persons. For this purpose I only employed those 20 test-persons of whom it could with certainty be assumed that they had no disturbances of the intellect, and ascertained how many could in each case identify a particular phase. If a phase is recognized by at least 14 test-persons (70 %, that is), this performance must be regarded as characteristic for a normal person. We then find the following:

TABLE II.

Recognized with:	Matchbox	Key	Bottle	Button	Scissors	Spoon	Wire-nail
Flannel							
6 layers	**15 tp.—75$^0/_0$**	9 tp.	13 tp.	7 tp.	3 tp.	3 tp.	5 tp.
5 „	17 „	**14 „ —70$^0/_0$**	**14 „ —70$^0/_0$**	8 „	5 „	8 „	11 „
4 „	18 „	16 „	16 „	8 „	9 „	10 „	11 „
3 „	19 „	19 „	17 „	11 „	**14 „ —70$^0/_0$**	**16 „ —80$^0/_0$**	11 „
2 „	19 „	20 „	20 „	**14 „ —70$^0/_0$**	17 „	19 „	**15 „ —75$^0/_0$**
1 layer	20 „	20 „	20 „	19 „	20 „	20 „	18 „
not recognized	——	——	——	1 tp.	——	——	2 tp.

It is here seen that the matchbox was recognized by 75 % of the test-persons even in its most difficult phase, which must be taken to indicate that this test is too easy. This objection does not apply to the other objects, only the bottle displays the peculiarity that the most indistinct phase is recognized by 13 test-persons, whilst the critical 70 % is only reached with the following phase. The lack of a sharp transition is a draw-back which renders this test also one of the least successful. The other objects however satisfy all demands that we are in the habit of making upon them.

It has now to be determined whether this experiment with the wrapped-up objects does really form an imagination-test. With this object I determined the correlation between the results of this test on the one hand and those with the hazy photographs, or the making of words from "droom" on the other hand. Of the hazy photographs 6 series of 6 pictures, representing 1^0. a horse, 2^0. a church, 3^0. a mill, 4^0. a dog, 5^0. a bicycle, and 6^0. a ship were used. For the very reason that the correlation is a measure of the relation of the number of common factors to the total number that have been active in both tests, it is not necessary to exclude the disturbances of intellect from this determination. As it happens, the 24 test persons who, owing to fortuitous circumstances, were all that could be used for the correlation calculation, recognized on the average 19.4 of the 36 pictures, which agrees fairly well with the results of SCHULTE and of ARKEMA, both of whom found that a recognition of about half the pictures could be counted on. 23 test-persons were able to take part in the tests in which words were made from "droom": they found an average of 9.4 in 3 minutes, an exceptionally good performance, that is. I now found the following correlations:

Wrapped-up objects — hazy photographs: $r = +0.23$.
Wrapped-up objects — words from "droom": $r = +0.46$.

Although the latter correlation is satisfactory, we cannot rest content with this result, as there is an insufficient connection between the apparently parallel tests of the hazy photographs and of the wrapped-up objects, to permit of our assuming that they measure the same function. It is therefore necessary in the first place to ascertain whether both the photographs test and the "droom" test are to be regarded as imagination-tests. The performances of the test-persons in both tests meet the demands which can per definitionem be made. For the imagination is the function by means of which given ideational complexes are analysed into their elements and new combinations are built up out of these elements. When the word "droom" — apart from its meaning — is seen as a combination of letters, and from these letters other words with quite different meanings are formed, work is performed which agrees well with this definition. But the completion of an indistinct perception with various elements which make an intelligible whole with what has been given, as is done in the case of the test with the hazy photographs, is also an operation of the imagination in the sense just indicated. We have therefore in the second place to enquire whether a sufficient degree of connection exists between the results of the two tests. That this connection is not wanting has already been shown by the investigations of SCHULTE and of ARKEMA, but, as already stated, the extent of the correlation was not shown by their method. I therefore calculated the correlation according to BRAVAIS-PEARSON in the case of 23 test-persons:

Hazy photographs — words from "droom": $r = +0.08$.

This correlation is seen to be absolutely inadequate, from which we may conclude that only one of the two tests is to be regarded as a real imagination test, but that the other, although the imagination has some share in the result, is mainly influenced by other factors. In order, then, to determine which test is directed chiefly to the imagination, I made a comparison with the results of the judgment-tests which were obtained with the aid of the above-mentioned absurd pictures, and calculated the correlation of the results of both tests with that of the absurd pictures, in this case, too, with 23 test-persons.

Hazy photographs — absurd pictures: $r = -0.02$.
Words from "droom" — absurd pictures: $r = +0.34$.

The first correlation is negative, but so low that we may safely assume that practically no connection exists between these two tests. The test of the absurd pictures — in which the critical faculty is the chief thing — meets very well the demands which may be made on a test of judgment; with the hazy photographs, on the other hand, the judgment apparently plays no part whatever. This latter experiment is thus the one that is to be regarded as purely a test of the imagination. It is quite a different matter with the making of words from "droom"; the fairly high correlation with the absurd pictures shows that in this test the judgment is a not unimportant factor, of even much greater significance than the imagination. Nor is this so very strange, for the alteration of the order of 5 letters undoubtedly demands a certain power of imagination, but is still a very simple operation, the combinations of letters so found must, however, be judged critically. The test-person has to ask himself whether they have any meaning and whether he has not already mentioned the word before, and he also has to take care that a letter which does not occur in the word "droom" may not have crept by accident into his words. We can therefore, by analysing more closely the performance required of the test-person, readily understand that in this test the judgment must be of importance.

If now we return to our wrapped-up objects, the question arises whether the fairly high correlation with the making of words from "droom" may not be due to the fact that the judgment is an important factor in the first test also. We can discover this by determining the correlation between the results of the tests with the wrapped-up objects and with the absurd pictures. This was also done with 23 test-persons.

Wrapped-up objects — absurd pictures: $r = +0.26$.

We see that this correlation is, it is true, not sufficient to justify our regarding the object-test as a test of judgment, but that it nevertheless has a certain significance. It is even seen that judgment and imagination are in this test of about equal importance. At first sight this may seem surprising, since there seems to be an absolute parallelism between the hazy photographs which give the test-person ever-distincter visual perceptions, and the wrapped-up objects, with which it is tactile perceptions which constantly become clearer, but I believe that the fact is to be explained. Human beings are wont to live principally in visual perceptions. They have in this way learned to interpret their visual impressions immediately. With tactile impressions this is not the case. A perception comes about by our arranging the separate sensations and combining them into a particular image. From childhood we have practised this, so far as our visual sensations are concerned, so that we immediately recognize a certain form even in indistinct combinations, and have no need to ask ourselves consciously what we really see. On the other hand such an indistinct image will require certainly some amplification, for which we have to call in the aid of our imagination. In our tactile sensations, however, we are nothing like so much at home; if they are indistinct, we shall certainly, owing to lack of practice in this direction, have to make great efforts to try to realize what we really feel and exactly what shape corresponds to our impressions. In addition to this, we are able, as it were, to take in at one glance a picture that is not too large, whereas when feeling a package we get a number of consecutive impressions which combined have to form our perception. We therefore have first to judge our touch-impressions, as accurately as possible to determine to what shape they correspond, before the second phase, the amplification of the imperfect image by means of the imagination, can begin. In view of this, therefore, it is clear that in the test with the wrapped-up objects the activity of the imagination is preceded by an activity of the judgment, which is of equal importance for the bringing about of the final result. With the test of the hazy photographs, however, this activity of the judgment has become so easy owing to the tremendous amount of practice which we have all had in the course of our life with respect to our visual perceptions, the judgment comes about so rapidly and so very unconsciously, that this function is of no more importance for the result of the test. The difference between the two tests is, I think, sufficiently accounted for in this way.

With this, then, the place of the test with wrapped-up objects amongst our other intellect-tests is indicated. They do not form a test with which one particular element of the intellect can be investigated, but they certainly have a value as an intellect-test in general. The functions of judgment and of imagination are of about equal importance for the result. Of the separate objects which were used, the matchbox and the bottle were found to be the least suitable, all the others, however, were very suitable; the key should be identified when wrapped in five layers of flannel, the scissors and the spoon when packed in three layers, the button and the wirenail, finally, when surrounded by two layers.

The tests of the hazy photographs and of the absurd pictures proved to have practically no common factors; the former is to be regarded as a pure imagination-test, the latter as a measure for the judgment.

Finally, the making of as many words as possible from "droom" proved to demand an imagination-element, but to be dependent to a much greater extent on a well-developed judgment.

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Hydrodynamics. — *On the application of* OSEEN's *theory to the determination of the friction experienced by an infinitely thin flat plate.* By J. M. BURGERS. (Mededeeling N⁰. 16 uit het Laboratorium voor Aero- en Hydrodynamica der Technische Hoogeschool te Delft). (Communicated by Prof. H. A. KRAMERS).

(Communicated at the meeting of June 28, 1930).

1. In a previous paper an example has been given of the treatment of a hydrodynamical problem with the aid of the equations given by OSEEN. The case considered belonged to the most simple class of problems, in which the fluid is bounded neither by exterior nor by interior surfaces, but is moving only under the influence of a system of external forces.[1]

The application of these equations to the determination of the motion of a fluid along a given body is more difficult. The question arises whether we can reduce the latter problem to a problem of the former class by substituting for the body an appropriate system of external forces. The introduction of such a system of forces proved to be of use in discussing the formula for the resistance experienced by a body;[2] in the case now before us we have to investigate how we can determine the magnitude and the distribution of these forces, by applying the condition that the velocity vanishes with sufficient accuracy in the points formerly occupied by the surface of the body (the body is at rest in a current of fluid and the motion is supposed to be stationary). Of course the problem of the convergence of the successive approximations now assumes a very difficult character, as the velocities to be produced by these forces are not small compared to the velocity of the original motion. However, as the first approximation has been investigated very extensively both by OSEEN and by others, it seems worth while to give some attention also to the second approximation.

As a preliminary example we propose to consider the most simple case: the motion of a fluid along an infinitely thin flat plate, lying parallel to the direction of the original current. In this case we may try to substitute for the plate a system of forces, directed tangentially, the magnitude of which has to be determined in such a way that the velocity vanishes in all points which were formerly occupied by the plate. The problem in itself is not new. The case of small REYNOLDS' numbers has been treated by BAIRSTOW, CAVE and LANG; they used the same method as the one indicated here, and considered the first approximation only.[1] The case of high REYNOLDS' numbers has been treated by BLASIUS, who used PRANDTL's equations for the motion within the boundary layer.[2] BLASIUS developed his approximations very far, and his results are well confirmed by experimental investigations. Though we cannot materially add to his results — our second approximation still falls rather short of BLASIUS' numbers — we hope that the following calculations will not be regarded as wholly superfluous, as they afford an example of what can be obtained by applying OSEEN's equations to boundary layer problems.

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[1] Cf. these Proceedings **32**, p. 1278, 1929 and also a paper to be published in the Zeitschr. f. angew. Math. u. Mechanik of this year.

[2] Cf. these Proceedings **33**, p. 504, 1930.

2. The field of motion is twodimensional; the coordinates are indicated by x_1, x_2. In the points of the segment of the x_1-axis defined by $0 \leqslant x_1 \leqslant l$ (to be denoted as the line l) forces are acting in the direction of this axis with the intensity $f(x_1)$ per unit of length. The velocity at infinity has the value V and is directed parallel to the axis Ox_1. The components of the velocity in an arbitrary point of the field will be denoted by $V + u_1$, u_2; they have to fulfill the conditions:

$$u_1 = -V, \qquad u_2 = 0 \qquad \text{at the line } l \quad . \quad . \quad . \quad . \quad (1)$$

The second condition of course is satisfied automatically on account of the symmetry of the field.

We write ϱ for the density of the fluid, ν for the kinematical coefficient of viscosity. REYNOLDS' number for the plate then becomes: $R = Vl/\nu$; further we put $k = V/2\nu$. The expressions for the components u_1, u_2 have the form:[3]

$$\left.\begin{aligned} u_1 &= \frac{1}{2\pi\varrho V}\iint d\xi_1\, d\xi_2 \left[Y_1 \left\{ \frac{V}{\nu}\varepsilon - \frac{\partial}{\partial x_1}(lg\, r + \varepsilon) \right\} - Y_2 \frac{\partial}{\partial x_2}(lg\, r + \varepsilon) \right] \\ u_2 &= \frac{1}{2\pi\varrho V}\iint d\xi_1\, d\xi_2 \left[-Y_1 \frac{\partial}{\partial x_2}(lg\, r + \varepsilon) + Y_2 \frac{\partial}{\partial x_1}(lg\, r + \varepsilon) \right] \end{aligned}\right\} \quad . \quad (2)$$

where $r = \sqrt{(x_1 - \xi_1)^2 + (x_2 - \xi_2)^2}$ and:

$$\varepsilon = e^{k(x_1 - \xi_1)} K_0(kr) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The quantities Y_i are given by the formula:

$$Y_i = X_i + y_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where the X_i represent the actual external forces — i. e. in our case the forces $f(x_1)$ —, while the y_i, the "apparent" or "interior" forces, are determined by the expressions:

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[1] L. BAIRSTOW, B. M. CAVE and E. D. LANG, Philos. Trans. London A **223**, p. 406, 1923.

[2] H. BLASIUS, Thesis Göttingen 1907 (Zeitschr. f. Math. u. Physik **56**, p. 1, 1908).

[3] C. W. OSEEN, Hydrodynamik (Leipzig 1927), p. 37. — The notation used in the text is the same as was used in these Proceedings **33**, p. 504.

$$y_1 = + \varrho\, u_2\, w, \qquad y_1 = - \varrho\, u_1\, w \quad . \; . \; . \; . \; . \; . \; . \qquad (5)$$

Here w is the vorticity, given by:

$$w = \frac{\partial u_2}{\partial x_1} - \frac{\partial u_1}{\partial x_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (6)$$

3. *First approximation.* We neglect the quantities y_i, and put: $Y_1 = f$, $Y_2 = 0$. Then the formula for u_1 becomes:

$$u_1 = \frac{1}{2\pi\varrho V} \int_0^l d\xi_1\, f(\xi_1) \left[\frac{V\varepsilon}{\nu} - \frac{\partial}{\partial x_1} (lg\, r + \varepsilon) \right] \quad . \; . \; . \; . \qquad (7)$$

moreover we have to substitute zero for ξ_2 in the expression for r.

We apply this formula to the points of the line l; then also x_2 is zero, and we get the integral equation for the function f:

$$\left. \begin{aligned} & \frac{1}{2\pi\varrho V} \int_0^l d\xi_1\, f(\xi_1) \left[\frac{V}{\nu} e^{k(x_1-\xi_1)} K_0 (k \mid x_1 - \xi_1 \mid) - \right. \\ & \qquad \left. - \frac{\partial}{\partial x_1} \{ lg \mid x_1 - \xi_1 \mid + e^{k(x_1-\xi_1)} K_0 (k \mid x_1 - \xi_1 \mid) \} \right] = - V \end{aligned} \right\} . \qquad (8)$$

Solutions of this equation have been obtained by BAIRSTOW, CAVE and LANG by means of a numerical method for the cases $kl = 2$ $(R = 4)$ and $kl = 20000$ $(R = 40000)$. It was assumed that the function f was constant over a number of intervals of the line l (in the case $kl =$ 20000, however, it proved necessary to assume another form for this function in the end intervals); the integral equation then could be reduced to a system of ordinary linear equations. From BAIRSTOW's results we quote the following values for the resistance W:

$$R = \quad 4 \ldots W = - \int_0^l d\xi_1\, f(\xi_1) = 6{,}108\ \mu V$$

$$R = 40\,000 \ldots W = \qquad\qquad 465{,}6 \quad \mu V.$$

We pass over to the case of great REYNOLDS' numbers. When $k \mid x_1 - \xi_1 \mid$ is greater than a definite number we may substitute for the K_0-function its asymptotic expansion; then the expression between [ ] in formula (8) becomes:

$$\text{for } x_1 > \xi_1: \quad \sqrt{\frac{\pi V}{\nu (x_1 - \xi_1)}} - \frac{1}{x_1 - \xi_1} + \frac{1}{4} \sqrt{\frac{\pi\nu}{V (x_1 - \xi_1)^3}} + \quad . \; . \; . \; . \qquad (9^a)$$

$$\text{for } x_1 < \xi_1: \quad - \frac{1}{x_1 - \xi_1} - \frac{1}{2} \sqrt{\frac{\pi\nu}{V (\xi_1 - x_1)^3}}\, e^{-2k(\xi_1 - x_1)} + \; . \qquad (9^b)$$

It is to be seen that as soon as $V(x_1-\xi_1)/\nu$ lies above a certain limit, the first term of (9) will be the only important quantity. We shall denote this limit by Vm/ν; even when it is taken equal to 2000 the interval m will be very small compared to the length l, provided R is sufficiently high, e.g. 100.000 or more. So we are induced in stead of the expressions (9^a), (9^b) to consider the approximations:

$$\text{for } x_1 > \xi_1: \qquad \sqrt{\frac{\pi V}{\nu(x_1-\xi_1)}} \qquad \text{. . . . . (10}^a)$$

$$\text{for } x_1 < \xi_1: \qquad 0 \qquad \text{. . . . . (10}^b)$$

It has to be remarked that both the expressions (10^a), (10^b) and the full expression between [ ] in formula (8) are integrable in the vicinity of the point $\xi_1 = x_1$: the full expression here becomes only logarithmically infinite. In the interval $x_1 - m < \xi_1 < x_1 + m$ we shall write χ for the difference between the actual value of the expression between [ ] in (8) and the approximation (10^a), (10). Then we put:

$$u_1 = u_0 + u' + u'' + u''' \qquad \text{. . . . . (11)}$$

where:

$$u_0 = \frac{1}{2\pi\varrho V}\int_0^{x_1} d\xi_1\, f(\xi_1)\sqrt{\frac{\pi V}{\nu(x_1-\xi_1)}} \qquad \text{. . . . . . (12}^a)$$

$$u' = \frac{1}{2\pi\varrho V}\int_{x_1-m}^{x_1+m} d\xi_1\, f(\xi_1)\,\chi \qquad \text{. . . . . (12}^b)$$

$$u'' = -\frac{1}{2\pi\varrho V}\left(\int_0^{x_1-m} + \int_{x_1+m}^{l}\right) d\xi_1\, f(\xi_1)\frac{1}{x_1-\xi_1} \qquad \text{. . . (12}^c)$$

$$u''' = \frac{1}{2\pi\varrho V}\int_0^{x_1-m} d\xi_1\, f(\xi_1)\left\{\frac{1}{4}\sqrt{\frac{\pi\nu}{V(x_1-\xi_1)^3}} + \dots\right\}^{1)} \qquad \text{. (12}^d)$$

We begin by neglecting u', u'', u''', and replace equation (8) by:

$$u_0 = \frac{1}{2\pi\varrho V}\int_0^{x_1} d\xi_1\, f(\xi_1)\sqrt{\frac{\pi V}{\nu(x_1-\xi_1)}} = -\beta V \qquad \text{. . . (13)}$$

Here the parameter β has been introduced in order to facilitate the distinction between terms of the first and second orders later on. Equation

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1) The second term in formula (9*b*) can be totally neglected when $V(\xi_1-x_1)/\nu \geqq 2000$; so it has not been taken into account in (12*d*).

(13) is an integral equation of ABEL's type, which can be solved easily;[1] we obtain:

$$f(\xi_1) = -\frac{2\beta\varrho\sqrt{\nu V^3}}{\sqrt{\pi\xi_1}} \quad \ldots\ldots\ldots \quad (14)$$

Formula (14) gives us the first approximation to the solution of our problem for great REYNOLDS' numbers. Taking β equal to 1 we get:

$$f(\xi_1) = -1{,}13\,\varrho\sqrt{\frac{\nu V^3}{\xi_1}} \quad \ldots\ldots\ldots \quad (14^a)$$

When the value (14) is substituted into (12^b), (12^c), (12^d) it can be shown that the quantities u', u'', u''' all are of the order of magnitude $R^{-1/2}$; hence they will vanish when REYNOLDS' number is increased without limit. We may correct for the errors caused by neglecting these quantities by introducing a supplementary system of forces f' to be determined from the equation:

$$\frac{1}{2\pi\varrho V}\int_0^{x_1} d\xi_1\, f'(\xi_1)\sqrt{\frac{\pi V}{\nu(x_1-\xi_1)}} = -u' - u'' - u''' \quad \ldots \quad (15)$$

Proceeding in this way we may obtain an expression for the forces f in the form of a series arranged according to powers of $R^{-1/2}$. We shall leave aside, however, the calculation of this series, as the influence of the quadratic terms in the equations of hydrodynamics, which are represented by the "interior" forces y_1, y_2, is far more important.

Formula (14^a) gives for the total resistance experienced by the plate:

$$W = -\int_0^{l} d\xi_1\, f(\xi_1) = 2{,}26\,\mu V\sqrt{\frac{Vl}{\nu}} \quad \ldots\ldots \quad (14^b)$$

In the case $R = Vl/\nu = 40000$, which was mentioned before, we obtain from this formula $W = 451\,\mu V$, instead of the value $465{,}6\,\mu V$ as found by BAIRSTOW.

4. We accept the expression (14) and calculate the components of the velocity produced by the forces f. In order to do this with an appropriate degree of approximation, we have to consider what simplifications may be introduced into formulae (2).

The terms depending on $lg\,r$ may be described as follows: every force Y_1 acts as a negative source, of strength $-Y_1/\varrho V$, and every force Y_2 acts as a vortex of intensity $Y_2/\varrho V$.

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[1] Cf. e g. R. v. MISES u. PH. FRANK, Die Diff. u. Integralgleichungen der Mech. u. Physik (Braunschweig 1925) I, p. 391 (§ 2.1); E. T. WHITTAKER and G. N. WATSON, Modern Analysis (Cambridge 1920), p. 229 (§ 11. 8).

As to the terms depending on the function ε, we shall substitute for ε its asymptotic value:

$$\left.\begin{array}{ll}\text{for } x_1 > \xi_1: & \varepsilon = \sqrt{\dfrac{\pi\nu}{V(x_1-\xi_1)}}\, e^{-\frac{V(x_2-\xi_2)^2}{4\nu(x_1-\xi_1)}} \\ \text{for } x_1 < \xi_1: & \varepsilon = 0 \end{array}\right\} \quad \ldots\ldots \quad (16)$$

Besides we shall neglect $\partial\varepsilon/\partial x_1$ when it is not multiplied by V/ν. In this way the parts of u_1, u_2 which depend on ε become (inserting the value of f from (14)):

$$u_1^* = -\frac{\beta V}{\pi}\int_0^{x_1} d\xi_1 \frac{1}{\sqrt{\xi_1(x_1-\xi_1)}}\, e^{-\frac{Vx_2^2}{4\nu(x_1-\xi_1)}}$$

$$u_2^* = -\frac{\beta V}{2\pi}\int_0^{x_1} d\xi_1 \frac{x_2}{\sqrt{\xi_1(x_1-\xi_1)^3}}\, e^{-\frac{Vx_2^2}{4\nu(x_1-\xi_1)}}.$$

In the second formula we substitute $\xi_1 = x_1\sigma^2/(\sigma^2+1)$; after the substitution the integral can be solved at once. In order to obtain the first integral we observe that $\partial u_1^*/\partial x_2 = -Vu_2^*/\nu$. In this way we find:

$$u_1^* = -\beta V\left(1 - Erf\frac{V|x_2|}{2\sqrt{\nu x_1}}\right)$$

$$u_2^* = -\frac{\beta\sqrt{\nu V}}{\sqrt{\pi x_1}}\frac{x_2}{|x_2|}\, e^{-\frac{Vx_2^2}{4\nu x_1}},$$

where *Erf* denotes GAUSS' error function.

It is easily to be seen that the parts u_1^{**}, u_2^{**}, depending on $lg\, r$, become of the order of magnitude $f/\varrho V$, i.e. of the order $\beta\sqrt{\nu V/l} = \beta V/R^{1/2}$. Hence it appears that u_1^{**} may be neglected in comparison with u_1^*, while u_2^{**} and u_2^* are of the same order. We shall presently see that it is sufficient to consider only a region of very small thickness stretching out along the line l; in this region we find the value of u_2^{**} from the discontinuity that the row of sources with intensity $-f/\varrho V$ produces in the normal component of the velocity, and thus we have:

$$u_2^{**} = \mp\frac{f}{2\varrho V} = \frac{\beta\sqrt{\nu V}}{\sqrt{\pi x_1}}\frac{x_2}{|x_2|}.$$

Finally the values of u_1, u_2 become:

$$u_1 = -\beta V\left(1 - Erf\frac{V|x_2|}{2\sqrt{\nu x_1}}\right) \quad \ldots\ldots \quad (17)$$

$$u_2 = \frac{\beta\sqrt{\nu V}}{\sqrt{\pi x_1}}\frac{x_2}{|x_2|}\left(1 - e^{-\frac{Vx_2^2}{4\nu x_1}}\right) \quad \ldots\ldots \quad (18)$$

It is to be seen that u_2 vanishes for $x_2 = 0$. The expression for u_1 vanishes when x_2 takes values great compared to $\sqrt{\nu x_1 / V}$. The second formula then does not vanish; besides it takes an infinite value when x_1 approaches to zero. This would have been obviated if we had used the full expression for ε in stead of the asymptotic value. It may be remarked that in BLASIUS's calculations the component u_2 shows an analogous behaviour.

In calculating the vorticity by means of formula (6) we shall neglect the term $\partial u_2 / \partial x_1$. Then we get:

$$w \simeq -\frac{\partial u_1}{\partial x_2} = -\beta \frac{\sqrt{V^3}}{\sqrt{\pi \nu x_1}} \frac{x_2}{|x_2|} e^{-\frac{V x_2^2}{4 \nu x_1}} \quad . \quad . \quad . \quad . \quad (19)$$

Formulae (17)—(19) are valid only when $x_1 \leqq l$. Integrals expressing the values of u_1, u_2, w for values of x_1 greater then l are more complicated. We mention only the value of the vorticity w:[1])

$$w = -\beta \frac{\sqrt{V^3}}{\sqrt{\pi \nu x_1}} Erf \left(\frac{x_2}{2} \sqrt{\frac{V l}{\nu x_1 (x_1 - l)}} \right) . e^{-\frac{V x_2^2}{4 \nu x_1}} . \quad . \quad . \quad (20)$$

5. *Second approximation.* In order to calculate the corrections to be applied to the results given by the first approximation, we have to introduce the "interior" forces y_1, y_2, determined by formulae (5), and to find the motion these forces produce. It is to be seen that they are acting only in the narrow strip along the line l where there is vorticity. We shall restrict ourselves to the calculation of the correction to be applied to the component u_1 in the points of the line l.

Motion produced by the force $y_1 = + \varrho u_2 w$. We find from (18) and (19) for $0 < \xi_1 < l$:

$$y_1 (\xi_1, \xi_2) = \varrho u_2 w = -\frac{\beta^2 \varrho V^2}{\pi \xi_1} \left(e^{-\frac{V \xi_2^2}{4 \nu \xi_1}} - e^{-\frac{V \xi_2^2}{2 \nu \xi_1}} \right) . \quad . \quad . \quad (21)$$

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[1]) The value of u_1 can be deduced from this formula by means of an integration with respect to x_2. In the special case $x_1 = 2l$ the integration can be effected at once, and we get:

$$u_1 = -\frac{1}{2} \beta V \left[1 - \left(Erf \frac{x_2}{2} \sqrt{\frac{V}{2 \nu l}} \right)^2 \right] .$$

In the axis ($x_2 = 0$) this gives for the resultant velocity:

$$V + u_1 = V \left(1 - \frac{1}{2} \beta \right) .$$

This result is of some interest in connection with calculations by S. GOLDSTEIN on the distribution of the velocity in the wake behind the plate (Proc. Cambr. Philos. Soc. 26, Part I, p. 18, 1930). GOLDSTEIN starts from PRANDTL's equations and obtains about 0,66 V for the velocity at a distance l behind the rear edge of the plate (comp. fig. 2 of his paper).

This expression has to be substituted for Y_1 into formula (2). As we have:

$$\int d\xi_2\, y_1 = -\frac{\beta^2 \varrho \sqrt{\nu V^3}}{\sqrt{\pi \xi_1}} (2 - \sqrt{2}),$$

it can be shown that the part of u_1 depending on $lg\, r$ becomes of the order $\beta^2 \sqrt{\nu V / l} = \beta^2 V / R^{1/2}$ and can be neglected.

As to the terms depending on ε, we again neglect $\partial \varepsilon / \partial x_1$ where it is not multiplied by V/ν, and substitute for ε the asymptotic value (16). Taking regard of the circumstance that now $x_2 = 0$, we obtain:

$$\left.\begin{aligned} \bar{u} &= -\frac{\beta^2 V^{3/2}}{2\, \pi^{3/2} \nu^{1/2}} \int_0^{x_1} d\xi_1 \int_{-\infty}^{+\infty} d\xi_2 \frac{e^{-\frac{V x_1 \xi_2^2}{4\nu (x_1 - \xi_1) \xi_1}} - e^{-\frac{V (2 x_1 - \xi_1) \xi_2^2}{4 \nu (x_1 - \xi_1) \xi_1}}}{\xi_1 \sqrt{x_1 - \xi_1}} = \\ &= -\frac{\beta^2 V}{\pi} \int_0^{x_1} \frac{d\xi_1}{\sqrt{\xi_1}} \left(\frac{1}{\sqrt{x_1}} - \frac{1}{\sqrt{2 x_1 - \xi_1}} \right) = -\beta^2 V \left(\frac{2}{\pi} - \frac{1}{2} \right) \end{aligned}\right\} . \quad (22)$$

Motion produced by the force $y_2 = -\varrho u_1 w$. From (17) and (19) we obtain for $0 < \xi_1 < l$:

$$y_2 (\xi_1, \xi_2) = -\varrho\, u_1\, w = -\frac{\beta^2 \varrho V^{5/2}}{\sqrt{\pi \nu \xi_1}} \left\{ \frac{\xi_2}{|\xi_2|} - Erf \frac{\xi_2 \sqrt{V}}{2 \sqrt{\nu \xi_1}} \right\} e^{-\frac{V \xi_2^2}{4 \nu \xi_1}}. \quad (23)$$

which expression has to be substituted for Y_2 into formula (2). In order to calculate the term depending on $lg\, r$, we consider the system of vortices with intensities $y_2 / \varrho V$. This system is symmetrical with respect to the line l, and we easily obtain:

$$\int_0^{\infty} d\xi_2\, y_1 = -\frac{1}{2} \beta^2 \varrho V^2.$$

From this result we immediately deduce that the system of vortices produces a velocity:

$$\bar{\bar{u}}' = -\frac{1}{2} \beta^2 V \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (24^a)$$

in the points of the line l.

Next we have to calculate the part depending on ε. This part is given by the integral:

$$\left.\begin{aligned} \bar{\bar{u}}'' &= +\frac{\beta^2 V^2}{4 \pi \nu} \int_0^{x_1} d\xi_1 \int_{-\infty}^{+\infty} d\xi_2 \frac{|\xi_2| - \xi_2\, Erf \frac{\xi_2 \sqrt{V}}{2 \sqrt{\nu \xi_1}}}{\xi_1^{1/2} (x_1 - \xi_1)^{3/2}} e^{-\frac{V x_1 \xi_2^2}{4 \nu (x_1 - \xi_1) \xi_1}} = \\ &= \frac{\beta^2 V}{\pi x_1} \int_0^{x_1} d\xi_1 \left(\frac{\sqrt{\xi_1}}{\sqrt{x_1 - \xi_1}} - \frac{\sqrt{\xi_1}}{\sqrt{2 x_1 - \xi_1}} \right) = \frac{1}{\pi} \beta^2 V \end{aligned}\right\} . \quad (24^b)$$

6. Adding together the amounts $\bar{u}$, $\bar{\bar{u}}'$, $\bar{\bar{u}}''$, we get for the correction deduced from the second approximation:

$$\bar{u}+\bar{\bar{u}}'+\bar{\bar{u}}''=-\beta^2 V\,.\,\frac{1}{\pi} \quad . \; . \; . \; . \; . \; . \; . \quad (25)$$

It is of interest to remark that this value, like that of u_0, does not depend on x_1. This is a consequence of the substitution of the asymptotic value for the function ε; it can be shown in a general way that in all approximations calculated on this basis u_1 becomes a function of the variable $x_2/\sqrt{x_1}$ only, while u_2 is a function of this variable, multiplied by $1/\sqrt{x_1}$.

Taking together now the amounts given by (13) and (25) and adding to the result the general velocity V, we obtain for the velocity in the points of the line l:

$$V+u_0+(\bar{u}+\bar{\bar{u}}'+\bar{\bar{u}}'')=V\left(1-\beta-\frac{1}{\pi}\beta^2\right) \quad . \; . \; . \quad (26)$$

In order to make this vanish, we have to take:

$$\beta=0{,}80 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (27)$$

Hence the expression for the force in the second approximation retains the form (14); substituting for β its value (27), we now get:

$$f(\xi_1)=-0{,}90\,\varrho\sqrt{\frac{\nu V^3}{\xi_1}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (28)$$

According to BLASIUS's calculations the frictional force, experienced by one side of an infinitely thin plate per unit area has the value:

$$\tau=0{,}332\,\varrho\sqrt{\frac{\nu V^3}{\xi_1}}\,.$$

Taking the two sides together, we obtain:

$$2\tau=0{,}664\,\varrho\sqrt{\frac{\nu V^3}{\xi_1}}\,.$$

Hence the value given by (28) appears to be still 36 % too high. A comparison with formula (14^a) moreover shows that the convergence is not rapid.

In order to proceed further in this way it would be necessary to develop the expressions for the corrected values of u_1 and u_2 in the whole field (or rather in all points of the narrow strip lying along the line l). The integrals, however, become too clumsy to be readily evaluated.

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Astrophysics. — *On the electrostatic field of the sun due to its corpuscular rays.* By H. P. BERLAGE Jr., Weltevreden. (Communicated by Prof. H. A. KRAMERS).

(Communicated at the meeting of June 28, 1930).

In the space surrounding the sun there exists no doubt an electric field, for it has been shown that the sun emits electrically charged corpuscular rays which produce the auroras and the magnetic storms. The study of cosmogony has convinced me that it will be impossible to understand the evolution of the planets so long as we are not better informed about the electric field of the sun. I have therefore tried on previous occasions to establish the general properties of this field at least as far as it may be considered as stationary [1]). The individual and only temporary phenomena, as for instance the auroras and the magnetic storms which may be regarded as more or less violent changes in the normal situation, thus remain out of consideration. In the following note I will discuss the results of my last attempt to solve the problem.

The nature of the particles of which the corpuscular rays of the sun consist, has not yet been completely explained. Thus far it has apparently not been possible from the character of the auroras and magnetic storms to establish unambiguously the nature of the projectiles which penetrate into the earths atmosphere. Astrophysics provide us with far better indications. According to the researches of E. A. MILNE it is rather probable that the particles in question consist of *Ca*-ions and electrons, but for the following a nearer specification is not needed.

Our only assumption will be that the sun emits particles of two different kinds, viz. particles of mass m_p carrying one elementary positive charge and particles of mass m_n carrying one elementary negative charge. A stationary state can exist only when equal numbers of positive and negative particles leave the sun pro second and pass also through any sphere with the sun at its centre. Moreover we assume that the sun emits these particles equally distributed in all directions, in other words that there exists spherical symmetry.

Denoting the velocities of the positive and the negative particles by v_p and v_n resp., their distances from the sun by r, the radiation-force acting on them at a distance r by $S_p : r^2$ and $S_n : r^2$ resp., the surplus of positive charge, that lies within a sphere of radius r, by E, the mass of the sun by M and the gravitational constant by f, we find the following equations of motion:

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[1]) Versuch einer Entwicklungsgeschichte der Planeten, Gerlands Beiträge zur Geophysik, Bd. 17, 1927. Ergänzungsheft. Notiz zu meiner Kosmogonie, idem Bd. 18, 1928, Heft 2.

$$S_p - f M m_p + E e = m_p r^2 \frac{d}{dt} v_p = \tfrac{1}{2} m_p r^2 \frac{d}{dr} v_p^2 \tag{1}$$

$$S_n - f M m_n - E e = m_n r^2 \frac{d}{dt} v_n = \tfrac{1}{2} m_n r^2 \frac{d}{dr} v_n^2 \tag{2}$$

E will depend on v_p and v_n. Calling the positive and negative specific space-charge ϱ_p and ϱ_n resp. and denoting the number of positive and negative particles which pass per second through a sphere with radius r by n, we obtain the following relations:

$$4 \pi r^2 v_p \varrho_p = n e \tag{3}$$

$$4 \pi r^2 v_n \varrho_n = n e \tag{4}$$

From these relations we find in the first place:

$$v_p \varrho_p = v_n \varrho_n \tag{5}$$

and further:

$$\frac{dE}{dr} = 4 \pi r^2 (\varrho_p - \varrho_n) = n e \left(\frac{1}{v_p} - \frac{1}{v_n} \right) \tag{6}$$

Differentiating equations (1) and (2) with respect to r, we get:

$$e \frac{dE}{dr} = m_p r \frac{d}{dr} v_p^2 + \tfrac{1}{2} m_p r^2 \frac{d}{dr^2} v_p^2 \tag{7}$$

$$- e \frac{dE}{dr} = m_n r \frac{d}{dr} v_n^2 + \tfrac{1}{2} m_n r^2 \frac{d^2}{dr^2} v_n^2 \tag{8}$$

Eliminating E and r we find:

$$n e^2 \left(\frac{1}{v_p} - \frac{1}{v_n} \right) = m_p r \frac{d}{dr} v_p^2 + \tfrac{1}{2} m_p r^2 \frac{d^2}{dr^2} v_p^2 \tag{9}$$

$$- n e^2 \left(\frac{1}{v_p} - \frac{1}{v_n} \right) = m_n r \frac{d}{dr} v_n^2 + \tfrac{1}{2} m_n r^2 \frac{d^2}{dr^2} v_n^2 \tag{10}$$

I am not competent to ascertain whether a general solution of this set of simultaneous differential equations can be obtained, but fortunately our problem is of such a kind that an approximate solution can be found by limiting ourselves to the electrostatic field at a large distance from the sun.

Equation (6) shows that v_p and v_n will be equal to each other at infinity In fact if with increasing r the quantity dE/dr approached a finite limit instead of zero, logarithmic potentials would occur, causing the velocity of the particles of one kind to increase without limit and forcing the particles of the other kind to return at a finite distance. This disagrees with the assumption of a stationary state; consequently the limiting velocities of the positively and negatively charged particles are equal. We will denote this limiting velocity by v_0. Beyond a certain distance r_0 from the sun $v_p - v_n$ will be small, and in this region we have:

$$v_p \sim v_n \sim v_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

Dividing (9) by m_p and (10) by m_n and substracting the second equation from the first, we get:

$$\left.\begin{aligned} n e^2 \left(\frac{1}{m_p} + \frac{1}{m_n}\right) \frac{v_p - v_n}{v_p\, v_n} + r \frac{d}{dr} (v_p - v_n)(v_p + v_n) + & \\ + \tfrac{1}{2} r^2 \frac{d^2}{dr^2} (v_p - v_n)(v_p + v_n) = 0 & \end{aligned}\right\} \quad (12)$$

This leads according to (11) in the first approximation to:

$$\frac{n e^2}{v_0^3} \left(\frac{1}{m_p} + \frac{1}{m_n}\right)(v_p - v_n) + 2\, r \frac{d}{dr} (v_p - v_n) + r^2 \frac{d^2}{dr^2} (v_p - v_n) = 0 \quad (13)$$

Posing:

$$\frac{n e^2}{v_0^3} \left(\frac{1}{m_p} + \frac{1}{m_n}\right) = a \quad . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

the general solution of (13) becomes:

$$v_p - v_n = r^{-1/2} \{ c_1\, r^{\sqrt{1/4 - a}} + c_2\, r^{-\sqrt{1/4 - a}} \} \quad . \; . \; . \; . \quad (15)$$

Substituting in (6) we find:

$$\frac{dE}{dr} = - \frac{n e}{v_0^2} r^{-1/2} \{ c_1\, r^{\sqrt{1/4 - a}} + c_2\, r^{-\sqrt{1/4 - a}} \} \quad . \; . \; . \; . \quad (16)$$

Integrating this from a lower limit r_0, we obtain

$$E = - \frac{n e}{v_0^2 a} \left[r^{1/2} \{ c_1 (\tfrac{1}{2} - \sqrt{\tfrac{1}{4} - a})\, r^{\sqrt{1/4 - a}} + c_2 (\tfrac{1}{2} + \sqrt{\tfrac{1}{4} - a})\, r^{-\sqrt{1/4 - a}} \} \right]_{r_0}^{r} + E_0 \quad (17)$$

where E_0 denotes the positive charge within a sphere of radius r_0. *The electrostatic fieldstrength at a distance r is given by* $E : r^2$.

For the sake of completeness we have still to express the constants of integration v_0, c_1 and c_2 in terms of the known quantities. Adding (1) and (2) and integrating the resulting equation, we get:

$$\{ S_p + S_n - f M (m_p + m_n) \} \left(\frac{1}{r_0} - \frac{1}{r} \right) = \tfrac{1}{2} m_p (v_p^2 - v_1^2) + \tfrac{1}{2} m_n (v_n^2 - v_2^2) \quad (18)$$

where v_1 and v_2 represent the velocities of the positive and negative particles on passing the surface r_0. We will consider them as known quantities. The common limiting velocity of the two kinds of particles follows therefore from:

$$\frac{S_p + S_n - f M (m_p + m_n)}{r_0} = \tfrac{1}{2} (m_p + m_n)\, v_0^2 - \tfrac{1}{2} m_p\, v_1^2 - \tfrac{1}{2} m_n\, v_2^2. \quad (19)$$

A first relation between c_1 and c_2 is deduced from equation (15) and has the form:

$$v_1 - v_2 = c_1\, r_0^{-1/2 + \sqrt{1/4 - a}} + c_2\, r_0^{-1/2 - \sqrt{1/4 - a}} \quad . \quad . \quad . \quad . \qquad (20)$$

To determine c_1 and c_2 separately we need still a second relation between them which can be found by integrating (1) or (2) between the limits r_0 and ∞. The integration of (1) leads to:

$$\left.\begin{array}{l} \dfrac{S_p - f\,M\,m_p + E_0\,e}{r_0} - \dfrac{ne^2}{v_0^2 a}\displaystyle\int_{r_0}^{\infty}\Big\{c_1\left(\tfrac{1}{2} - \sqrt{\tfrac{1}{4} - a}\right) r^{-3/2 + \sqrt{1/4 - a}} + \\ + c_2\left(\tfrac{1}{2} + \sqrt{\tfrac{1}{4} - a}\right) . \, r^{-3/2 - \sqrt{1/4 - a}}\Big\}\, dr + \dfrac{n\,e^2}{v_0^2 a}\Big\{c_1\left(\tfrac{1}{2} - \sqrt{\tfrac{1}{4} - a}\right) r^{1/2 + \sqrt{1/4 + a}} + \\ \qquad + c_2\left(\tfrac{1}{2} + \sqrt{\tfrac{1}{4} - a}\right) r^{1/2 - \sqrt{1/4 - a}}\Big\}\displaystyle\int_{r_0}^{\infty}\frac{dr}{r^2} = \tfrac{1}{2}\, m_p\,(v_0^2 - v_1^2), \end{array}\right\} \qquad (21)$$

or:

$$\left.\begin{array}{l} \dfrac{S_p - f\,M\,m_p + E_0\,e}{r_0} - \dfrac{m_p\, m_n}{m_p + m_n}\, v_0 \Big\{c_1\left(\tfrac{1}{2} + \sqrt{\tfrac{1}{4} - a}\right) r_0^{-1/2 + \sqrt{1/4 - a}} + \\ \qquad + c_2\left(\tfrac{1}{2} - \sqrt{\tfrac{1}{4} - a}\right) r_0^{-1/2 - \sqrt{1/4 - a}} = \tfrac{1}{2}\, m_p\,(v_0^2 - v_1^2) \end{array}\right\} . \qquad (22)$$

We have thus solved the following problem. When through a sphere with radius r_0 surrounding the sun positive and negative particles are passing with velocities differing only little from their limiting velocities and when the radiation-force acting upon them and the total charge within the sphere r_0 are given, it is required to find the specific space-charge and electrostatic fieldstrength at a distance $r > r_0$ from the sun.

The solution has a very curious property. It is evident from (15) that we must distinguish between two cases: $a < \frac{1}{4}$ and $a > \frac{1}{4}$. When $a < \frac{1}{4}$ the right side of (15) is a real function of r and also the following equations contain only real terms. In this case v_p and v_n approach each other in an aperiodical way and E and the fieldstrength $E : r^2$ behave as monotonous functions.

When $a > \frac{1}{4}$ we get, applying the EULERian transformations, instead of (15), (16) and (17) the following formulae:

$$v_p - v_n = r^{-1/2}\left\{c_1 \cos\left(\sqrt{a - \tfrac{1}{4}}\, \log\frac{r}{r_0}\right) + c_2 \sin\left(\sqrt{a - \tfrac{1}{4}}\, \log\frac{r}{r_0}\right)\right\} \qquad (23)$$

$$\frac{dE}{dr} = -\frac{n\,e}{v_0^2}\, r^{-1/2}\left\{c_1 \cos\left(\sqrt{a - \tfrac{1}{4}}\, \log\frac{r}{r_0}\right) + c_2 \sin\left(\sqrt{a - \tfrac{1}{4}}\, \log\frac{r}{r_0}\right)\right\} \qquad (24)$$

$$\left.\begin{array}{l} E = -\dfrac{n\,e}{v_0^2 a}\Bigg[r^{1/2}\Big\{\left(\tfrac{1}{2}\, c_1 - c_2\sqrt{a - \tfrac{1}{4}}\right) \cos\left(\sqrt{a - \tfrac{1}{4}}\, \log\dfrac{r}{r_0}\right) + \\ \qquad + \left(c_1\sqrt{a - \tfrac{1}{4}} + \tfrac{1}{2}\, c_2\right) \sin\left(\sqrt{a - \tfrac{1}{4}}\, \log\dfrac{r}{r_0}\right)\Big\}\Bigg]_{r_0}^{r} + E_0 \end{array}\right\} . \qquad (25)$$

This solution has a periodical character. When the distance from the sun increases, we find alternate regions where $v_p > v_n$ and $v_n > v_p$. In one spherical shell the positive particles overtake the negative ones whereas in the next shell the negative particles in their turn will overtake the positive ones. Due to this the space-charge in the successive concentric spherical shells is alternately positive and negative. One might speak of the nodes and the anti-nodes of the field. The ratio between the radii r_n and r_{n+1} of two successive nodal spheres is a constant:

$$\frac{r_{n+1}}{r_n} = e^{\frac{\pi}{\sqrt{a - {}^1/_4}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The question then arises what governs the value of the constant a which determines whether the solution is periodic or aperiodic. Formula (14) shows that a is the only constant which contains n, the number of positive and negative projectiles that leave the sun pro second, a being proportional to n. Thus if the corpuscular current is only small, the velocities of the positive and negative particles approach each other in a monotonous way. When the current increases, however, and exceeds a certain critical value, we encounter the above mentioned nodal spheres. On the surface of these spheres the difference between the two velocities changes its sign, although the maximal difference obviously decreases in outward direction.

It would no doubt be very interesting to know the value of a for the sun. Indeed — returning for a moment to cosmogony — if a were larger then ${}^1/_4$, then (26) would be valid which reminds us strongly of the approximatively constant ratio of the radii of two successive planetary orbits. This seems to suggest a connection of some kind. In a second communication I will return to the question whether such a connection is conceivable.

SUMMARY.

An approximate analytical expression is found for the charge density and force of the electrostatic field at great distances from the sun, if it may be assumed that one kind of positively charged and one kind of negatively charged particles are radially expelled in space by the sun and are leaving it in equal and stationary amounts in all directions.

Different solutions occur in the two cases that the stream of charged corpuscles is weak or strong. The second solution suggests cosmogonic consequences which will be investigated in a succeeding paper.

Weltevreden, May 1930.

Chemistry. — *Die Komplexität des Phosphorpentoxyds*, II. Von A. SMITS (Nach Versuchen zusammen mit H. W. DEINUM).

(Communicated by Prof. P. ZEEMAN).

Zur Erklärung des höchst eigentümlichen Verhaltens des Phosphorpentoxyds wollen wir, ebenso wie es bei Phosphor, Schwefelsaurem Anhydrid etc. geschah, die meist einfache Annahme machen, dass das pseudo-System von P_2O_5 aus zwei Pseudokomponenten besteht, welche sich stark in Flüchtigkeit von einander unterscheiden.

Wenn wir dieses machen, so kommen wir zu dem Schluss, dass das System P_2O_5 nicht so kompliziert ist, wie das System Schwefelsaures Anhydrid, weil keine einzige Erscheinung gefunden worden ist, welche auf eine Verbindung in dem System P_2O_5 hinweist. Das äusserst merkwürdige Verhalten des P_2O_5 kann vollkommen erklärt werden durch die P,T-Figur des Pseudosystems, welche in Figur 9 angegeben ist.

a und b sind die Tripelpunkte der α und β Pseudokomponenten. Die mit $S_\alpha + G$ angegebene Linie ist die Sublimationskurve der reinen α; und so ist die mit $S_\beta + G$ angedeutete Linie die Sublimationskurve der reinen β Pseudokomponente; ac ist die Dreiphasenlinie für die Koexistenz von α-Mischkristallen + Flüssigkeit + Dampf und bc ist die Dreiphasenlinie für die Koexistenz von β-Mischkristalle + Flüssigkeit + Dampf; c ist der Quadrupelpunkt. Weiter ist cf die Dreiphasenlinie für α-Mischkristalle, β-Mischkristalle und Flüssigkeit und so ist gc die Dreiphasenlinie für α-Mischkristalle, β-Mischkristalle und Dampf.

Die P,T-Figur des unären Systems ist nun (siehe die Theorie der Allotropie, Seite 24) 1) in diesem Pseudo-System gelegen und ist in unserer Figur mit schweren Linien angegeben. $B'BC$ ist die Dampfdruckkurve der unären Flüssigkeit, d.h. der Flüssigkeit in innerem Gleichgewicht. Diese Kurve begegnet in B der Dreiphasenlinie für $S_{\beta_M} + L + G$, so dass BB' metastabil ist und der Punkt B den unären stabilen Tripelpunkt von P_2O_5 darstellt, welches bei 55,5 cM. Hg und 580° gelegen ist. BD ist die unäre Schmelzlinie. Wenn die unterkühlte Flüssigkeit sich unär verhalten könnte bis zu B', wo die unäre metastabile Dampfspannungskurve der verlängerten Dreiphasenlinie für $S_{\alpha_M} + L + G$ begegnet, und wenn dann die Kristallisation einträte, würde die metastabile unäre Modifikation, also die flüchtige Form in innerem Gleichgewicht, erscheinen. Aber das ist nicht möglich, weil die innere Transformationen erst bei 400° bemerkbar werden.

---

1) In der Theorie der Allotropie ist hier den Fall „Enantiotropie" betrachtet. — Weil es aber hier bei P_2O_5 vollkommen gleichgültig ist. Monotropie oder Enantiotropie anzunehmen, ist hier der einfachste Fall, nämlich Monotropie, vorausgesetzt.

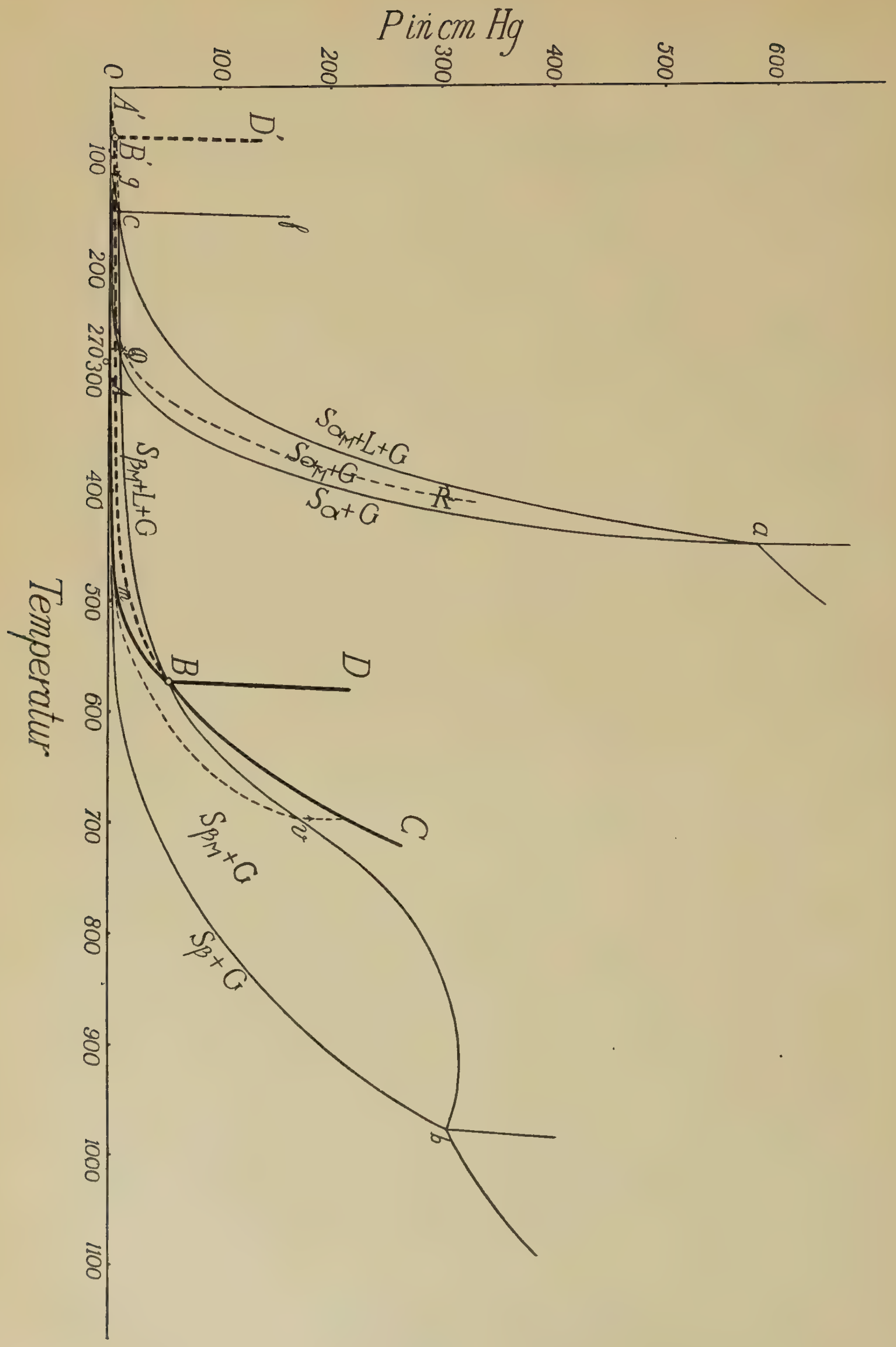
P in cm Hg
0
100
200
300
400
500
600
Temperatur
100
200
270°
300
400
500
600
700
800
900
1000
1100
A'
B'
D'
g
c
f
Q
A
$S_{\alpha M}+L+G$
$S_{\alpha M}+G$
$S_{\alpha}+G$
R
a
$S_{\beta M}+L+G$
n
B
D
v
C
$S_{\beta M}+G$
$S_{\beta}+G$
b

Fig. 9.

Jetzt wollen wir anfangen mit der Erklärung des Phenomens, dass wenn wir von der stabilen Modifikation bei 400°, also von der wenig flüchtigen Form in innerem Gleichgewicht bei 400° ausgehen und wir erhitzen nicht unsagbar langsam, oder besser, wir halten die Temperatur nicht jedes Mal längere Zeit konstant, sondern wir lassen die Temperatur z.B. 100° in 20 Minuten steigen, gar keine Schmelzung beobachtet wird, bevor 700° erreicht ist.

Diese Erscheinung lässt sich jetzt einfach hierdurch erklären, dass weil die innere Transformationen, welche bei 400° erst gut bemerkbar werden, selbst unterhalb 700° noch nicht schnell stattfinden, bei der genannten Temperatursteigerung das innere Gleichgewicht der Temperatur nicht folgen kann und der Stoff sich wie eine Mischkristallphase bestimmter Zusammensetzung verhält.

Was man dann beobachten wird, lässt sich ableiten aus dem $(P,T)_x$-Durchschnitt der pseudo- P,TX-Raumfigur, wobei dann x die obengenannte Zusammensetzung ist. Diesen Durchschnitt kann man sofort angeben bei Benutzung der Projektion der Dreiphasenstreifen des „pseudobinären" und der Zweiphasenstreifen des unären Systems auf die T,x-Ebene. (Siehe die Theorie der Allotropie, Seite 18), welche in Figur 10 angegeben ist.

Die Zweiphasenstreife des unären Systems sind hier, wie gewöhnlich, durch schwere Linien angegeben. Wie ersichtlich, ist hier Monotropie angenommen. Aus dieser Figur, welche sofort verständlich ist, folgt, dass die Lage der unären, stabilen Modifikation in Gleichgewicht mit ihrem Dampf bei der Temperatur von 400° durch den Punkt m angegeben wird. Wenn wir diesen Stoff nicht äusserst langsam erhitzen, so kann das innere Gleichgewicht, wie gesagt, der Temperatur nicht folgen und wenn wir schnell erhitzen, durchläuft der Stoff einen Durchschnitt, welcher mit der Zusammensetzung von m übereinstimmt. Dieser $(PT)_x$-Durchschnitt hat nun wie aus der Projektion Fig. 9 erhellt, die Gestalt, welche in Fig. 11 verzeichnet ist.

In dieser Figur sind alle Kurven, (die Kurve $o'q'$ ausgenommen) Grenzkurven zwischen Gebieten einer und zweier Phasen. Die Linie $o'q'$ ist die Dreiphasenkurve für $S_{\beta_M} + L + G$ und die Punkte $o'p'q'$ korrespondieren mit den Punkten $o'p'q'$ in Fig. 9. Diese Linien könnten mit derselben Zusammensetzung realisiert werden, wenn das Volumen willkürlich geändert werden könnte. Arbeitend bei konstantem Volumen, wie in unserem Fall, wird man eine Dampfdruckkurve finden, wie die punktierte Linie RV, derer Lage von dem Volumen abhängt.

Der Punkt V wurde zwar erreicht, doch weil dieser Punkt der Anfangsschmelzung erst bei ca 700°, also mehr als 100° oberhalb der Temperatur des unären stabilen Tripelpunkts, auftrat, bei welcher Temperatur die Geschwindigkeit der inneren Umsetzungen sehr merkbar zu genommen ist, stellt der Stoff sich hier in innerem Gleichgewicht, wobei der Druck steigt und die Dampfdrucklinie der unären Flüssigkeit erreicht

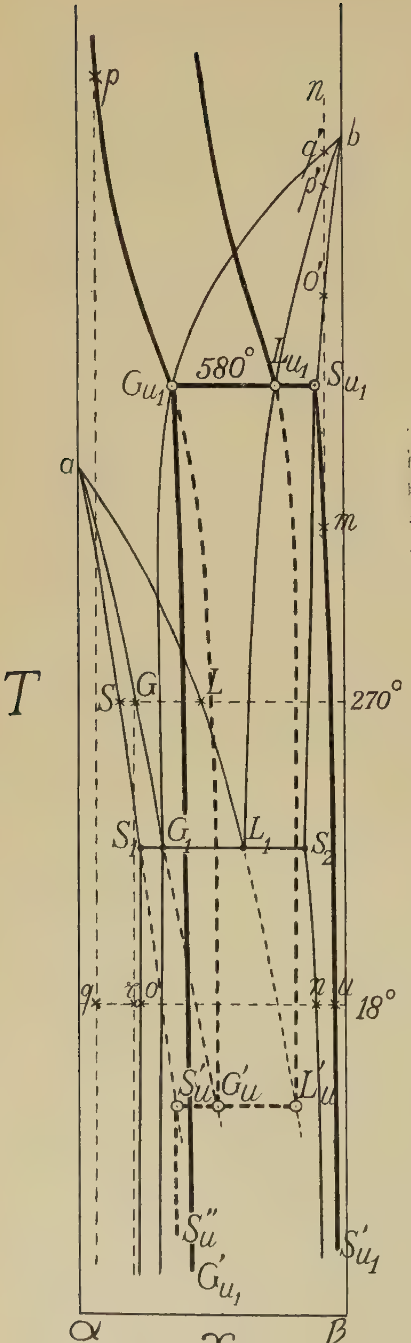

Fig. 10.

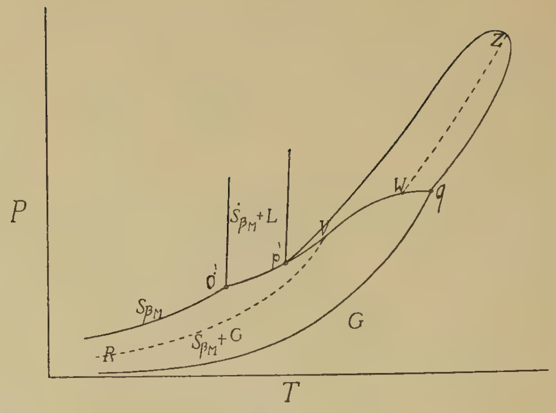

Fig. 11.

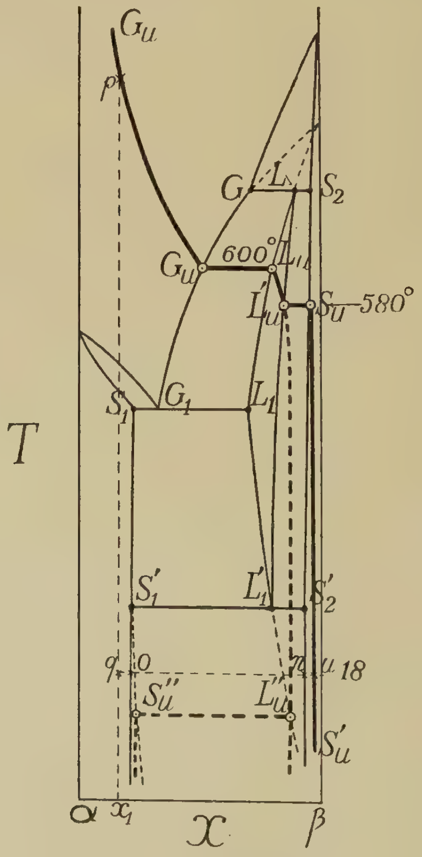

Fig. 12.

wird. Wenn wir denn auch in unserer P,T-Projektion Fig. 9, diese Dampfdruckkurve, welche bei schneller Erhitzung erhalten wurde, eintragen, so bekommen wir eine Linie, wie durch mV angegeben ist.

Es leuchtet ein, dass man bei weniger rascher Erhitzung in Folge der dann stattfindenden inneren Umsetzungen, während des Experimentes, allerlei Übergänge finden kann und bei viel niedriger Temperatur die Dreiphasenlinie für $S_{\beta_M} + L + G$ erreichen und einen Teil dieser Kurve realisieren kann.

Schreiten wir jetzt zu der flüchtigen Form des P_2O_5, so müssen wir erst die Frage zu beantworten versuchen, "was eigentlich das Handelsphosphorpentoxyd ist".

Wir dürfen hier annehmen, dass dieses P_2O_5 des Handels durch Verbrennung des Phosphors im Sauerstoff erhalten worden ist, wobei anfänglich dampfförmiges P_2O_5 von z.B. 1 Atm. und einer Temperatur von 800° entsteht. Durch rasche Abkühlung dieses Dampfes ist das bekannte Präparat entstanden.

Um zu sehen was dabei stattgefunden hat, ist es nötig einen $(TX)_P$ Durchschnitt durch unsere pseudo PT,X-Raumdarstellung, welche mit einem Druck von 1 Atm. korrespondiert, anzugeben.

Diesen Durchschnitt finden wir in Fig. 12.

Die schweren Linien geben hier wieder die Lage des unären Systems an. Wir sehen aus dieser Figur, dass, wenn der Stoff sich immer in innerem Gleichgewicht befand, der Dampf sich bei circa 600° (der unäre Siedepunkt) zu Flüssigkeit kondensieren und diese letzte bei 580° (dem unären Schmelzpunkt) zu der festen stabilen Modifikation erstarren wurde.

Unterhalb dieser Temperatur sollte die unäre Modifikation sich der Linie $S_u S'_u$ entlang bewegen und bei gewöhnlicher Temperatur den Punkt u erreichen. In metastabilem Zustand sollte die Flüssigkeit bei viel niedrigerer Temperatur zu der metastabilen Modifikation erstarren können.

Ganz andere Erscheinungen werden aber auftreten, wenn die Kühlung so rasch ist, dass die inneren Umsetzungen nicht stattfinden können und der innere Zustand des Dampfes fixiert wird. Wie Fig. 12 uns zeigt, bekommt man in diesem Fall bei gewöhnlicher Temperatur eine Mischkristallphase q, welche nicht in innerem Gleichgewicht ist und also keine Modifikation genannt werden kann.

Weil die inneren Umsetzungen selbst bei hoher Temperatur noch langsam stattfinden, wird eine solche Fixierung wahrscheinlich leicht auftreten können.

Doch muss man natürlich auch an die Möglichkeit denken, dass während der Abkühlung in den ersten Momenten eine geringe innere Umsetzung stattfindet und dass in Folge dessen die Totalzusammensetzung bei 18° in dem Gebiet für die Koexistenz von α und β Mischkristallen liegt.

In diesem Fall ist das Produkt ein Konglomerat von den zwei Mischkristallphasen o und n, aber es wird hauptsächlich aus α-Mischkristallen bestehen.

Es fragt sich jetzt, was geschehen wird, wenn man das Handels P_2O_5 bei 270° destilliert. Um diese Frage zu beantworten, betrachten wir den P, x-Durchschnitt, welcher mit 270° korrespondiert.

Dieses ist sofort aus Fig. 10 abzuleiten und wird durch Fig. 13 wiedergegeben.

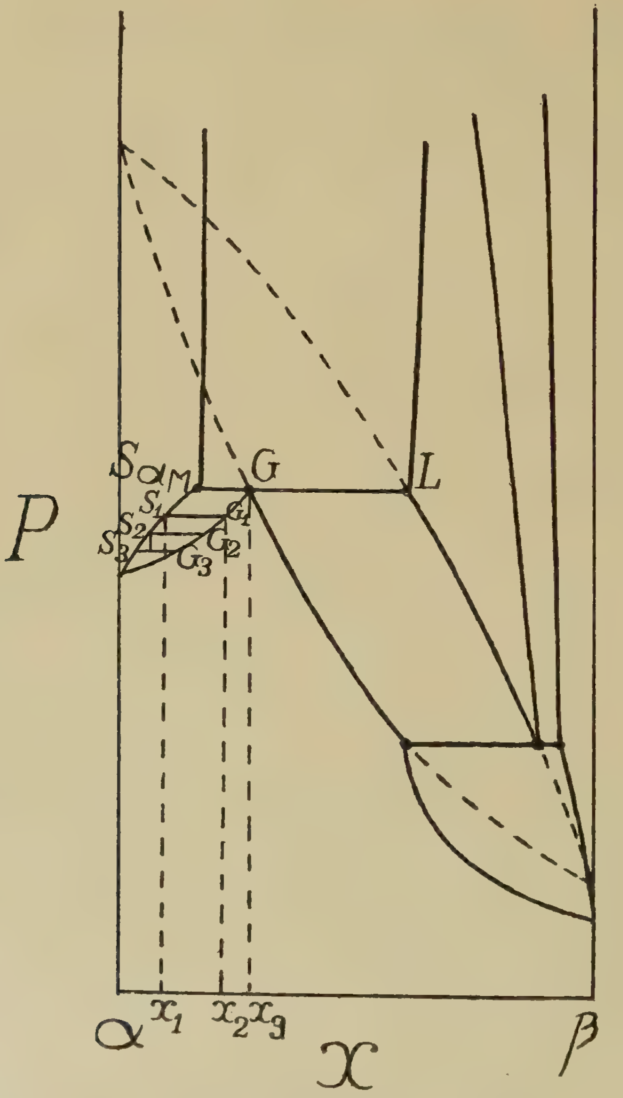

Fig. 13.

Erst wollen wir dann den Fall betrachten, dass das P_2O_5 des Handels eine homogene Mischkristallphase von der Zusammensetzung x_1 ist. Angenommen anfänglich koexistieren die Mischkristallphase S_2 und die

Gasphase G_2, dann können wir uns vorstellen, dass die Dampfphase plötzlich durch Kondensation weggenommen wird, so dass wir nur die Mischkristallphase S_2 zurückhalten. Nach einiger Zeit hat sich dann die Koexistenz zwischen der Mischkristallphase S_3 und der Gasphase G_3 eingestellt und wir denken uns dann diese Gasphase wieder plötzlich durch Kondensation abgeführt. So können wir uns den Destillationsprocess diskontinuierlich vorstellen und das Resultat ist also, dass man ein Destillat erhält, dessen Zusammensetzung zwischen 0 und x_2 liegt. Es leuchtet ein, dass die Zusammensetzung des Destillats nicht nur von der Zusammensetzung des P_2O_5 des Handels, sondern auch von der Fraktion, welche abdestilliert worden ist, abhängt. Destilliert man nicht in Vakuum, sondern in einem Sauerstoffstrom, wie in der Tat der Fall ist, so wird natürlich auch die Geschwindigkeit des Sauerstoffstromes einen Einfluss ausüben können, weil die Temperatur in Destillationsrohr bei steigender Geschwindigkeit des Sauerstoffstromes etwas sinken wird. Jedenfalls ist es evident, dass verschiedene Präparate im allgemeinen eine verschiedene Zusammensetzung und also, bei derselben Temperatur, einen anderen Dampfdruck besitzen werden.

Die zweite Möglichkeit ist, dass das P_2O_5 des Handels aus einem Konglomerat von α- und β-Mischkristallen, welches aber sehr reich an α-Mischkristallen ist, besteht. In diesem Fall wird bei 270° ein Dreiphasengleichgewicht zwischen α-Mischkristallen S, Dampf G und Flüssigkeit L bestehen. Bei der Destillation wird, so lange diese Dreiphasenkoexistenz bestehen bleibt, der Dampf G von der Zusammensetzung x_3 zu einer Mischkristallphase von derselben Zusammensetzung, oder zu einem Konglomerat von derselben Totalzusammensetzung kondensieren. In unserer T, x Projektion liegt diese Zusammensetzung bei 18° (Punkt r) noch in dem homogenen Mischkristallgebiet, aber es ist natürlich noch eine dritte Möglichkeit, dass nämlich die Zusammensetzung des Dampfes G bei gewöhnlicher Temperatur in dem Gebiet für die Koexistenz von α-und β-Mischkristallen liegt. Hierbei muss noch bemerkt werden, dass, wie weiter unten gezeigt werden wird, bei der Destillation die Flüssigkeit L verschwinden kann, und dass die Dreiphasenkoexistenz zwischen $S_{\alpha_m} + G + L$ in eine Zweiphasenkoexistenz $S_{\alpha_m} + G$ übergeht, wenn nämlich die Totalzusammensetzung des P_2O_5 des Handels, bei 270°, zwischen den Zusam- mensetzungen von S_{α_m} und G liegt, welches nicht unwahrscheinlich ist.

In diesem Fall wird dann das Destillationsprodukt fortwährend reicher an α werden, wie in dem zuerst vorausgesetzten Fall, wo das P_2O_5 des Handels nur eine α-Mischkristallphase ist.

Jetzt können wir eine Erklärung von der äusserst merkwürdigen Lage der Dampfspannungskurve der flüchtigen Form des P_2O_5 geben. Dazu werden wir erstens den Fall voraussetzen, dass das reine destillierte Präparat bei 18° eine homogene Mischkristallphase von der Zusammensetzung x_1 (siehe Fig. 13) ist.

Wir zeichnen dann den $(PT)_x$-Durchschnitt, welcher mit der Zusammensetzung x_1 korrespondiert; diese ist in Fig. 14 wiedergegeben. Aus dieser Figur sehen wir, dass die flüchtige Form eine Dampfdruckkurve liefern wird, welche in dem Gebiet für $S_{\alpha_M} + L$ liegen muss, derer Lage aber von dem Volumen abhängig ist. Die punktierte Linie QS gibt diese Dampfdruckkurve bei bestimmtem Volumen an. Diese Kurve konnte wegen der Umwandlung in der stabilen Modifikation, welche etwas oberhalb 400° auftritt, nicht bis Temperaturen oberhalb 400° verfolgt werden und deshalb ist ein Übergang auf die Dreiphasenlinie nicht beobachtet. So ist also die rätselhafte Lage der Dampfdruckkurve der flüchtigen Form erklärt.

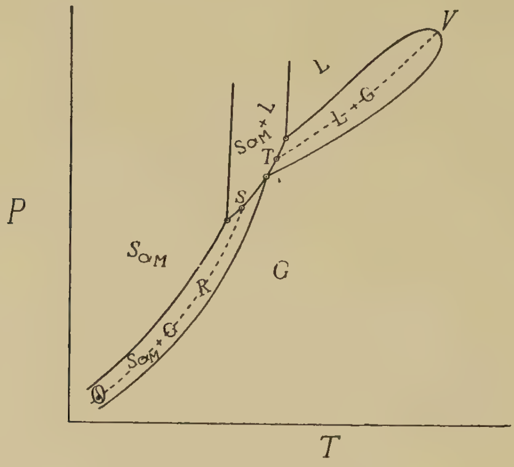

Fig. 14.

Wie schon gesagt, werden die verschiedenen Präparate der flüchtigen Form verschiedene Zusammensetzung besitzen und mit einer Änderung in der Zusammensetzung ist eine Änderung in der Dampfdruckkurve verbunden. So erklären sich also auch die gefundenen Dampfspannungsunterschiede bei den verschiedenen Präparaten.

Wie schon erwähnt, lässt sich bei einer partiellen Destillation der flüchtigen Form, ebenso wie das schon bei dem violetten Phosphor und bei der hochschmelzenden Asbestform des Schwefelsauren Anhydrids konstatiert worden ist, ein Rest erhalten mit einem viel niedrigeren Dampfdruck. Die Dampfdruckerniedrigung betrug, wie aus Tabelle II folgt, bis zu 20 % und wahrscheinlich wird der Effekt noch vergrössert werden können.

Diese Erscheinung lieferte uns den Beweis, wie schon gesagt, dass die flüchtige Form eine Mischkristallphase ist.

Nun haben wir aber an zweiter Stelle auf die Möglichkeit hingewiesen, dass das destillierte Produkt die Zusammensetzung x_3 hat (siehe

Fig. 13). Die $(PT)_x$-Figur für diese Zusammensetzung ist in Fig. 15 gegeben. Die Differenz mit Fig. 14 ist, wie ersichtlich, nur darin gelegen, dass die Dreiphasenlinie länger ist und dass der Punkt V bei 270° liegen muss und deshalb S noch niedriger. Weil die Dampfdruckmessungen der flüchtigen Form bei ungefähr 270° anfingen, wurde man also in diesem Fall die Dreiphasenlinie für $S_{\alpha_M} + L + G$ bestimmt haben. Oberflächlich betrachtet würde man denken können, dass dieser Fall sofort ausgeschaltet werden kann, weil doch gefunden worden ist, dass bei partieller Abdestillation ein Rest mit niedrigerem Dampfdruck erhalten werden kann, und das ist doch nicht möglich bei einem Dreiphasengleichgewicht.

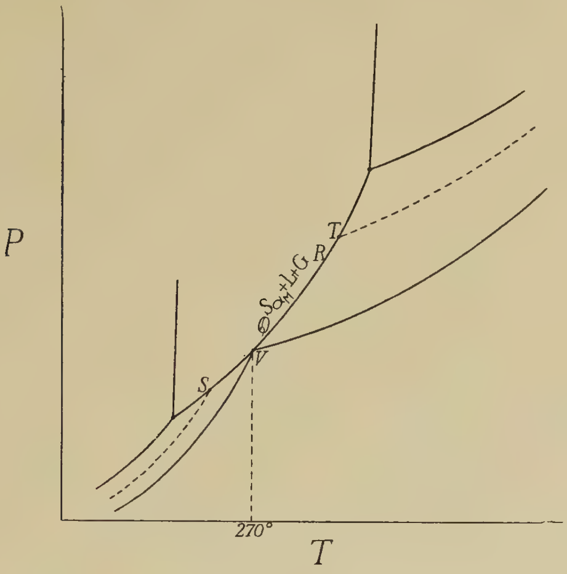

Fig. 15.

Es ist vollkommen richtig, dass dieses nicht möglich ist, so lange Dreiphasengleichgewicht besteht und darum ist zu überlegen, ob es möglich ist, dass wir bei der Destillation das Dreiphasengebiet verlassen und dann, was hier wichtig ist, in das Gebiet für die Koexistenz von Mischkristallen und Dampf treten.

Diese Frage lässt sich sofort beantworten bei der Betrachtung des V,x-Diagramms Fig. 16, welches mit einer Temperatur etwas unterhalb 270° korrespondiert.

In diesem V,x-Diagramm ist das Molekularvolumen als Funktion der Zusammensetzung dargestellt.

Es genügt hier nur zwei Gebiete zu betrachten, erstens das Gebiet für die Koexistenz von α-Mischkristallen, Dampf und Flüssigkeit, angegeben durch die einen Dreieck bildende Punkte S, G und L; und zweitens das Zweiphasengebiet für die Koexistenz von α-Mischkristallen und Dampf. Wir sehen, dass wenn die Totalzusammensetzung zwischen den

Zusammensetzungen der Punkte S und G liegt und z.B. x_1 ist, während das Volumen V_1 beträgt, der Zustand des Dreiphasensystems durch p angegeben wird. Wenn wir nun durch G und p eine Gerade ziehen, so wird diese Gerade die Linie SL in n begegnen. Hieraus lässt sich schliessen, dass das System aus pn gr. mol Dampf und Gp gr. mol Fest + Flüssig besteht.

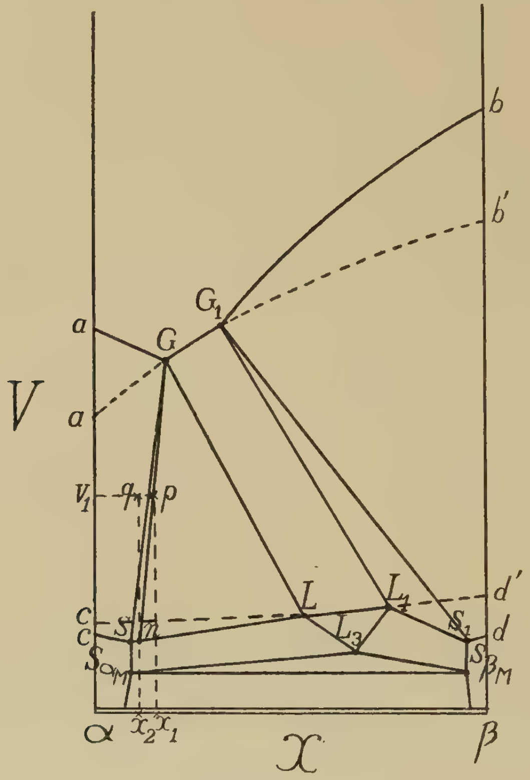

Fig. 16.

Der Process der Destillation kann nun diskontinuierlich betrachtet werden in der Weise, dass der Dampf plötzlich vollkommen separiert und kondensiert wird, sodass nur Fest + Flüssig übrig bleibt, angegeben durch den Punkt n, welcher mit der Zusammensetzung x_2 korrespondiert. Bringen wir jetzt das Volumen wieder auf den anfänglichen Wert, v_1, so ist der Zustand durch den Punkt q gegeben, woraus folgt, dass wir jetzt in das Zweiphasengebiet für α-Mischkristalle und Dampf getreten sind.

Diese Erscheinung ist, wie ersichtlich, nur möglich, wenn die Totalzusammensetzung anfänglich zwischen den Punkten G und S liegt und dann wird es also möglich sein, dass, wenn man anfänglich das Dreiphasengleichgewicht zwischen α Mischkristallen, Dampf und Flüssigkeit misst, nach einer genügenden Abdestillation eine Dampfdruckerniedrigung auftritt, weil wir in das Zweiphasengebiet für α-Mischkristalle und Dampf getreten sind. Nun ist es aber wahrscheinlich, dass die $\frac{dp}{dT}$ der Dreiphasenlinie deutlich kleiner sein wird, als die $\frac{dp}{dT}$ der Zweiphasenlinie, $S_{\alpha_M} + G$ in demselben Temperaturtrajekt nach der Abdestillation. In der Tatsache, dass die gefundenen Linien einander praktisch parallel gehen, liegt also eine Anweisung, dass die feste flüchtige Form auch bei Temperaturen bis zu 400° nur aus α-Mischkristallen besteht. Dieses ist vollkommen sicher, wenn die kleinste Abdestillation genügt um eine Dampfdruckerniedrigung zu realisieren. In der nächsten Abhandlung werden die Resultate der Destillationsversuchen, des Restes und des Destilates betreffend, und noch diejenige der Röntgenuntersuchungen und der Dampfdichte-bestimmungen mitgeteilt werden.

Zum Schluss sei hier bemerkt, dass also das reine destillierte P_2O_5, das ohne Zweifel die meist trockne Substanz ist, die wir kennen, ihre Komplexität auf ausserordentlich deutliche Weise zeigt, weil die inneren Transformationen erst dicht unter 400° merkbar werden und die Substanz sich deshalb unterhalb dieser Temperatur, wie ein Gemisch verhält.

Das Entstehen und das Bestehen der flüchtigen Form mit ihrer ausserordentlich merkwürdig gelegenen Dampfdruckkurve ist dem *Ausbleiben* der inneren Umwandlungen zwischen der verschiedenen Molekülarten, unterhalb genannter Temperatur, zuzuschreiben. Und ohne Zweifel ist das Ausbleiben der inneren Umwandlungen bis zur dieser relativ hohen Temperatur dem extrem grossen Trocknungsgrad des destillierten P_2O_5 zu verdanken.

Man hat darum allen Grund zu erwarten, dass, wenn es gelingt andere Substanzen durch P_2O_5 so stark zu trocknen, dass sie den gleichen Trocknungsgrad, wie P_2O_5 selbst erreicht haben, viele dieser Substanzen sich bis zu einer gewissen Temperatur wie ein Gemisch verhalten, und so ihre Komplexität auf meist überzeugende Weise verraten werden.

ZUSAMMENFASSUNG.

Es wurde die schon früher von SMITS und RUTGERS gefundene wunderliche Lage der Dampfdruckkurve der metastabilen flüchtigen Form bezüglich derjenigen der stabilen Modifikation des Phosphorpentoxyds bestätigt gefunden.

Die verschiedenen Präparate der flüchtigen Form gaben verschieden gelegene Dampfdruckkurven. Bei der Temperatur 400°, wobei die flüchtige Form anfängt sich deutlich in die stabile Modifikation umzuwandeln, beträgt der Dampfdruck 3 bis 3.5 Atm. und sinkt dann bei derselben Temperatur nach langem Warten bis unterhalb 1 cm Hg. Von der stabilen Modifikation lässt sich, durch bei jeder Temperatur so lange zu warten, bis die Substanz sich in innerem Gleichgewicht gesetzt hat, die unäre Sublimationskurve und ebenso die unäre Dampfspannungs-

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kurve der Flüssigkeit bestimmen und so wurde dann für den unären stabilen Tripelpunkt 55.5 cm Hg und 580° gefunden.

Es wurde gezeigt, warum die flüchtige Form, die wir kennen, nicht in innerem Gleichgewicht sein kann und also auch *nicht* eine Modifikation ist. Die innere Umsetzungen beginnen eben bei 400° anzufangen deutlich aufzutreten, aber dann bewirken diese eine Umwandlung in die stabile feste Phase. Die einzige andere Möglichkeit war, wie die theoretische Betrachtung zeigt, die Bildung einer unären, metastabilen Flüssigkeitsphase, aber das wurde nicht beobachtet.

Bei 400° ist die innere Gleichgewichtseinstellung noch so langsam, dass, wenn wir von 400° ausgehend die stabile Form rasch erhitzten, ein Beginn von Schmelzung erst mehr als 100° oberhalb des unären Tripelpunktes beobachtet werden konnte, welches am deutlichsten die Komplexität der stabilen Modifikation verriet und also zeigte, dass es ein Mischkristall ist, welcher sich bei unärem Verhalten in innerem Gleichgewicht befindet.

Dass auch die flüchtige Form, *welche sich niemals in innerem Gleichgewicht befindet*, ebenfalls eine Mischkristallphase ist, wurde bewiesen durch die Tatsache, dass durch eine partielle Abdestillation der Dampfdruck stark erniedrigt wird.

Unter Voraussetzung der Existenz von zwei Molekülarten, welche ein pseudobinäres System mit einem Eutektikum bilden, konnte dies alles an der Hand der Theorie der Allotropie, leicht erklärt werden, so wohl das Verhalten der *wenig flüchtigen Form* bei sehr langsamer und bei sehr rascher Erhitzung und die Möglichkeit einer mehr als 100° grossen Überhitzung dieses festen Stoffes, wie auch das Verhalten der *flüchtigen Form*, mit ihrer für die ältere Betrachtungsweise absolut unbegreiflichen Lage der Dampfspannungskurve.

Die neueren Betrachtungen zeigen, dass die flüchtige Form eine *α*-Mischkristallphase sein muss und dass diese Phase ihr Entstehen und Bestehen bis 400° daran dankt, dass unterhalb dieser Temperatur keine innere Umsetzungen stattfinden. Wenn die inneren Umsetzungen bei 400° einmal anfangen, dann ist es um die flüchtige Form geschehen, weil, wie die Betrachtungen zeigen, die metastabile Form in innerem Gleichgewicht unterhalb 270°, und wahrscheinlich tief darunter schon, ihr Tripelpunkt erreicht haben würde.

Der Stoff P_2O_5 zeigt uns also auf schönster Weise, wie wunderbare Erscheinungen auftreten können, wenn das innere Gleichgewicht sich nicht einstellt.

Mit der Theorie der Allotropie lassen sich diese Erscheinungen sofort erklären, weil diese Theorie einen sogenannten einfachen Stoffen wie ein, aus mehr Molekülarten zusammengesetzten Stoff, in innerem Gleichgewicht, auffasst und sich, unter Anderm damit befäst, die möglichen Lagen der unären Systems in dem Pseudosystem anzugeben. Man erhält dabei nicht nur eine tiefere Einsicht in den Zusammenhang der unären Phasen eines Stoffes, sondern auch in sein Verhalten, für den Fall das innere Gleichgewicht sich nicht oder langsam einstellt.

Die Anzahl der Stoffe, wobei man die Komplexität bewiesen hat, nimmt immer zu, und so wird es nicht lange mehr dauern, bis man zu der Erkennung kommen wird, dass im Allgemeinen jeder sogenannte einfache Stoff einem Pseudo-System angehört.

Laboratorium für allgemeine und anorganische
Chemie der Universität,

Amsterdam, Mai 1930.

Physics. — *Study of electrolytic dissociation in nitric acid by Raman effect.*

By I. RAMAKRISHNA RAO M. A., Ph. D., Bezwada Research Fellow of the Andhra University. (Communication from the Physical Institute of the University of Utrecht.) (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of June 28, 1930.)

1. *Introduction.*

In a previous communication the preliminary results of the study of electrolytic dissociation in nitric acid by the Raman effect have been published. As was mentioned therein, there was a strong continuous spectrum superposed on the Raman lines, in the elimination of which considerable error might have been made in evaluating the dissociation in nitric acid which was calculated from the intensities of the Raman line due to the NO_3-ion at various concentrations of the acid. Further work has revealed some more drawbacks in the previous method of investigation, which had to be overcome for arriving at more accurate values of the amount of dissociation. The purpose of the present communication is to describe the improvements and to record the results obtained therefrom.

It may not be out of place here to give in brief the actual observations which have led to the employment of the Raman effect in determining the dissociation in nitric acid. In the spectrum for this acid there are six Raman lines corresponding to infra-red characteristic wavelengths at 15.67, 14.60. 10.45, 9.56, 9.00, 7.69 μ accompanying each strong exciting line in the mercury vapour lamp. Of these the lines corresponding to 9.56 μ and 7.69 μ are the most intense. Spectra taken with $NaNO_3$, NH_4NO_3 and KNO_3 have shown three Raman lines of infra-red wavelengths 15.67, 14.60, 9.56 μ corresponding to each exciting mercury line. These three lines are in identical positions for nitric acid and nitrates. Study of the Raman Spectra with different concentrations of nitric acid in water has revealed two interesting features. The lines that are present in nitric acid as well as nitrates increase in intensity with diminishing concentration of the acid up to a certain stage and then diminish again. On the other hand, those that are present in nitric acid alone, but absent in the nitrates, progressively diminish in intensity until they become so feeble that they are scarcely noticeable at dilutions where the lines common to nitric acid and nitrates are very conspicuous. This phenomenon shows that the percentage of NO_3-ions which are common to nitric acid and nitrates, and which

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[1] Proc. Roy. Soc., (Lond.), A Vol. **127**, pp. 279—289, 1930.

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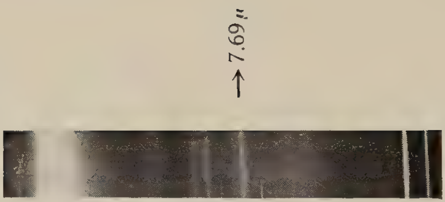
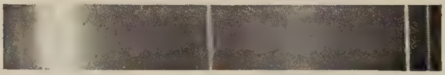
Fig. 1



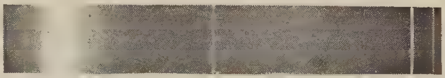
$15\ N\ HNO_3$

Fig. 2



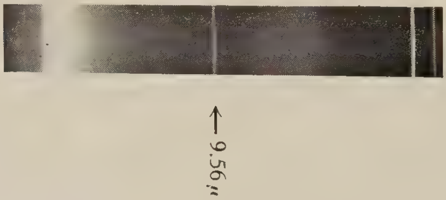
$6\ N\ NaNO_3$

Fig. 3



$6\ N\ NH_4NO_3$

Fig. 4



$6\ N\ HNO_3$

therefore give rise to the Raman lines corresponding to 15.67, 14.60 and 9.56 μ infra-red wavelengths, increase with dilution of the acid. This is obviously due to the dissociation of nitric acid with increasing dilution.

To give an idea of the phenomenon, Raman spectra for the various substances are given in the plate. Fig. 1 in the plate is the spectrum for nitric acid of concentration 15 N (15 gramme molecules in 1 litre of solution). Figs. 2 and 3 represent the spectra taken with $NaNO_3$ and NH_4NO_3 respectively, of concentration 6N each. Fig. 4 is for nitric acid of concentration 6N. The spectra 2, 3 and 4 are for the same times of exposure. But in the case of concentrated nitric acid the exposure is made longer to bring out clearly the fainter Raman lines. It is evident from these spectra that there is a strong line common to nitric acid at both concentrations and the nitrates. But 15 N nitric acid has in addition one strong and two weaker lines which are scarcely visible in the more dilute solution. In fact, the spectrum of dilute nitric acid is identical in appearance with that of the two nitrates and has less resemblance to the concentrated acid. This clearly proves that in the former solution there are very few of the undissociated HNO_3 molecules, which give rise to the additional Raman lines in the concentrated acid.

2. *Experimental Method.*

The method of obtaining Raman spectra is, in essentials, the same as that proposed by WOOD [1]). In the author's previous work [2]), the liquid to be studied was taken in a glass tube ending in a horn at one end and a uniform spherical bulb at the other. The form of the tube adopted is represented in Fig. 1. It was surrounded by a glass jacket (represented in dotted lines in the figures), through which cold water was circulated for cooling the liquid from the intense heat of the mercury vapour lamp, which was placed directly above the tube and as nearly along it as possible. The

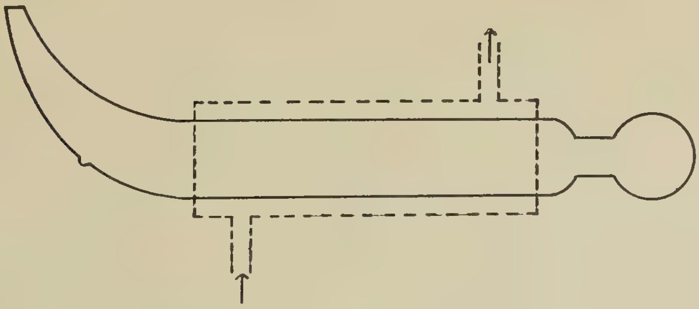


Fig. 1.

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[1]) Phil. Mag., Vol, 6, p. 729 (1928).

[2]) Loc. cit.

light scattered by the liquid was concentrated on the slit of the spectrograph by the liquid lens formed by the bulb of the glass tube. The horn at its other end was painted black so that all back-ground illumination was effectively cut off. For the exact collimation of the scattered light along the collimator of the spectrograph, the small glass bead melted on to the outside of the sloping wall of the horn along the axis of the tube was found to be very convenient. And for quantitative work of the type aimed at in this investigation, where the arrangement had to be kept under identical conditions for a number of different exposures, the bead was indispensable.

One serious drawback, which was later found out in this arrangement, was the deposition of a thin layer of salt on the inside of the top of the cooling jacket. On account of the intense local heating due to the mercury lamp, small air bubbles used to collect at the top of the jacket, and in the place where these bubbles were formed, the small amount of salt contained in the cooling water was gradually deposited thus forming a thin opaque layer which effectively cut off part of the light from the mercury vapour lamp. Thus the illumination of the liquid might not have been the same for exposures with different liquids. Hence a new type of cooling arrangement was devised in which this difficulty was got rid of.

The new arrangement will be clear from Fig. 2. It consists of a rectangular metal box with a square cross-section. Two cylindrical metallic tubes 3 cms. in length are soldered co-axially at the two square ends of the box so that the quartz tube containing the liquid under investigation could be passed through them and made liquid tight by rubber washers. The box was open at the top and the cooling water entered it through a narrow tube soldered at the bottom. A wider tube, which was soldered right through the bottom of the box, ended just below its inside top and served as the outlet. It was fixed on one side of the interior of the box so that it did not stand in the way of the quartz tube passing through the end- on brass tubes. Thus water entering at the bottom of the box covered the tube containing the liquid to be studied and passed out through the

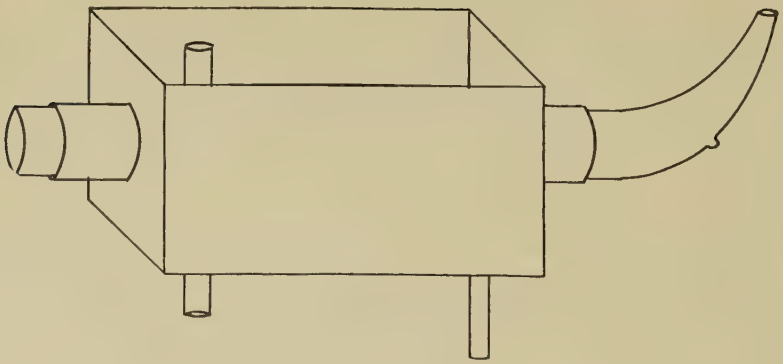


Fig. 2.

top of the second outlet tube whose upper end was about 3 mms. above the top of the quartz tube passing through the box. The mercury lamp was placed right above it and there was, in the space between the lamp and the tube, a sufficient layer of flowing water to effectively cut off all the heat from the arc.

This arrangement was doubly preferable to the previous cooling jacket. It automatically eliminated the formation of the opaque thin layer of salt between the mercury arc and the illuminated liquid. It also formed a plane layer of water instead of a cylindrical one between the two. Thus considerable backward reflection of the mercury arc light from the cylindrical surface of the cooling water jacket which might have reduced part of the incident light, was got rid of. Just below the tube containing the liquid and above the mercury arc, there were two well polished cylindrical aluminium reflectors which reflected all the light from the mercury arc into the liquid.

Another modification that was found necessary was the change of the spherical glass bulb in Fig. 1. The slight irregularities on its surface were sufficient to bring about non-uniform illumination of the slit. Also the lens formed by the bulb being neither achromatic nor anastigmatic, it was found necessary to discard it.

So the glass tube used in the previous work was substituted bij a quartz one which had at its end had optically plane quartz plate melted on to it. The light scattered by the liquid was focussed by means of an achromatic quartz-fluorite lens. The use of an additional lens no doubt cut off part of the feeble scattered light, but this only necessitated a little longer exposure. The new arrangement shown in Fig. 2 contains the quartz tube described above. This also ended in a horn with a small quartz bead melted on to its sloping outer wall exactly along the axis of the straight portion of the tube. Leaving the quartz bead the plane quartz plate at the other end of the tube, and a central portion of it equal in length to the length of the mercury arc, the whole of it is painted black to eliminate all extraneous light.

3. *Determination of the Electrolytic Dissociation in Nitric Acid.*

As has already been mentioned, nitric acid gives rise to two prominent Raman lines. One of them diminishes in intensity with increasing dilution of the acid. The other, which is found also in the Raman spectra for nitrates and which therefore corresponds to the NO_3-ion, increases in intensity at first with increasing dilution up to certain stage and then diminishes again in intensity with further dilution. This indicates that, on diluting the acid, the number of NO_3-ions increases at first more than in proportion to dilution, but later though the percentage of the NO_3-ions is larger, their concentration diminishes with dilution though not as quickly. Hence the increase at first in the intensity of the Raman line corresponding to this ion followed by progressive diminution.

The degree of dissociation, given by the proportion of the dissociated to the total number of nitric acid molecules, can therefore be determined either by studying the diminution in the intensity of the Raman line corresponding to the undissociated HNO_3 molecules or by measuring the change in the intensity of the NO_3-line. But there is one difficulty in the former case. The intensity of the Raman line corresponding to the undissociated molecule diminishes very rapidly with diminishing concentration. Very long exposures of the order of five to six hours are necessary to bring out these lines even at such large concentrations as 12 N. To go to higher concentrations is not possible because of the formation of nitrogen peroxide in the acid which brings about strong absorption in the acid to all colours on the short wavelength side beyond the blue, where alone it is easy to obtain measurable Raman spectra. Hence the measurement of the changes in the Raman corresponding to the undissociated molecules is not undertaken in this work.

On the other hand, the intensity of the NO_3-line is large even at small dilutions and in this work the measurement could be carried accurately up to 0.4 N solution of the acid. For work with still further dilutions very long exposures are necessary to get reliable data.

To determine the actual proportion of NO_3-ions at the different concentrations, it is necessary to find the intensity of the Raman line corresponding to them at each concentration under exactly identical conditions. To attain this the relative disposition of the tube containing the liquid with respect to the spectrograph must be kept constant for exposures with the different concentrations of the acid. Also the intensity of illumination of the mercury arc light incident on the liquid must be identical for all of them. For this purpose the distance between the lamp and the tube containing the liquid under investigation must be kept constant. Since the intensity of the mercury arc depends on the voltage and current, these also must be constant as far as possible. For studying the spectra with various concentrations of nitric acid under identical conditions the following procedure was adopted.

The rectangular metal box surrounding the quartz tube, through which the cooling water was circulated, was supported rigidly over a wooden stand and the quartz tube containing the liquid was fixed by two rubber washers through the two end-on brass tubes of the box. The small unpainted quartz bead was illuminated by a diffuse electric lamp and the wooden stand was so adjusted that the light from the bead, which appeared as a bright point source of light, passed through the plane quartz plate and through the slit of the spectrograph right along the collimator. It was fixed in a position where the bead appeared exactly in the centre of the camera lens of the spectrograph. Now an achromatic lens is introduced between the slit of the spectrograph and the tube containing the liquid. It is fixed in a position where it exactly focussed the bead on the slit. In this position the camera lens should be fully illuminated by the light from the bead. The lens and the spectrograph are now permanently fixed and left unchanged throughout all the exposures of Raman spectra with the different concentrations of nitric acid.

The mercury arc lamp is now placed above the quartz tube containing the liquid as nearly along it as possible. It is so arranged that after tilting for striking the arc, the quartz lamp was always in the same position with respect to the quartz tube.

A factor of uncertainty is the change in the refractive index of nitric acid with dilution. Because of this change the optical distance between the lens and the interior of the acid must also vary. Hence there may be a difference in the focussing of the scattered light on the slit of the spectrograph for different concentrations of the acid. This difference was clear from the change in the definition of the image of the quartz bead formed on the slit of the spectrograph, when the quartz tube was placed in identical positions, but with different acid concentrations. To see how far this difference bringes about change in the intensity of the scattered light that is incident on the slit of the spectrograph, spectra were taken with the same concentration of the acid under identical conditions but with slightly different distances between the lens and the tube. On finding the intensities of the Raman lines for the different positions of the quartz tube, the values were constant within the limits of experimental error. Thus the change in the refractive index, which brings about a difference in focussing of the scattered light similar to this, should not give rise to any appreciable change in the actual intensity of the scattered light that passes through the slit of the spectrograph.

The reason for this may be that the source of light in this case being diffuse and distributed over a large length and volume, may be equivalent to a parrallel beam of light, and hence slight changes in its distance from the lens may not give rise to any difference in the actual amount of scattered light falling on the spectrograph.

To decide the uncertainty further, spectra with the various concentrations were taken under two different dispositions of the tube. In one case no change was made in the position of the tube for the different concentrations. In the second, the lens was kept fixed as in the above case, and the position of the tube was changed until the image of the bead was exactly focussed on the slit for all concentrations. The mercury lamp was also shifted until its position relative to the quartz tube was identical for all the different exposures. A third set of intensity measurements with different concentrations was also made. In this, the tube and the mercury lamp were kept under identical conditions for all concentrations, but the position of the lens was changed till the bead was sharply focussed on the slit of the spectrograph. In all the three different cases, the intensity ratios of the Raman line of the NO_3-ion with the different concentrations of the acid were constant within the limits of experimental error. Hence it is concluded that the change in the refractive index did not bring about corresponding changes in the total intensity of scattered light that is focussed on the spectrograph.

As was pointed out in the previous communication, there was a conspicuous continuous spectrum which was superposed on the Raman lines. To eliminate this, the mercury lamp was burnt at a lower voltage by increasing the external resistance. Also the slit of the spectrograph was made narrower, both of which precautions effectively eliminated the continuous spectrum.

The mercury arc was burnt at the same voltage and current as far as possible for exposures with different concentrations of the acid. Each exposure was begun half-an-hour after the arc was struck to allow for the inconstancy of its intensity at the beginning. To allow for the changes in the voltage and current, readings of both were taken at intervals of fifteen minutes during the course of the exposures and correction made for the differences.

The temperature of the solutions was maintained constant to within 0.5° on either side of 14° C., so that there could not be any measurable change in the state of dissociation of the acid on account of variation of temperature.

The slit of the spectrograph was kept untouched and therefore absolutely constant in width during the exposures with the various concentrations.

Spectra with the different solutions of nitric acid were exposed on the same plate for exactly the same time, under identical conditions for all of them. Thus any changes in the intensities of the Raman lines in the spectra with the different concentrations must be due to changes in the number of molecules or ions giving rise to them and to no other circumstances.

4. *Intensity Measurements of the Raman Lines.*

To determine the intensities of the Raman lines for the various concentrations of the nitric acid, continuous spectra of known relative intensities are taken on the same plate. Light from a spiral filament lamp burning at constant voltage of twelve volts was allowed to pass along the slit of the spectrograph. By interposing an optically perfect lens between the source and the slit, a diffuse, but uniformly bright image of the filament is formed on the slit, so that over a centimeter width the illumination on either side was uniform. By increasing the width of the slit, the light passing through it into the spectrograph could be increased in a known proportion. Thus on the same plate, on which the Raman spectra with the different concentrations of the nitric acid were taken, continuous spectra with different slit widths were also made. The intensities of the latter were taken to be proportional to the slit widths.

By making microphotometric measurements of the densities of the continuous spectra at wave-lengths equal to those of the Raman lines whose relative intensities were to be determined, intensity-density curves were drawn for each plate. The densities of the Raman lines were also determined with the microphotometer and from these, their intensities were found from the intensity-density curves taken with the continuous spectra The intensity due to the small continuous spectrum, that was superposed on the Raman lines is eliminated from each. Thus the relative intensities of the Raman lines for the different concentrations of nitric acid were determined.

5. *Results.*

The results of the intensity measurements of Raman lines at λ 4226 and λ 4567 A.U. due to dissociated NO_3-ion are given in Table I. The spectra with 11.9, 10.2, ... 1.7 N concentrations of nitric acid were obtained with exposures of two and half hours each. Those with 0.85 and 0.42 N had to be exposed for five hours each to get measurable intensities of the Raman lines at such small concentrations. So two sets of different plates were taken, one with concentrations 11.9 N to 1.7 N and the other with 11.9, 1.7, 0.85, and 0.42 N. These had 11.9 N and 1.7 N concentrations in common for making the measurements with one plate comparable with those of the other. The results given in the Table are mean values obtained with four different sets of measurements. The variations in the actual values were 10 per cent on either side of the mean. Considering the difficulties of the intensity measurements and the various factors that bring about slight differences in the disposition of the apparatus with spectra taken with different concentrations of the acid, this variation is not much.

The first column in Table I gives the concentration in nitric acid in gramme molecules per one litre of the solution. The second contains the relative intensities of the Raman lines at λ 4226 A.U. corresponding to the different concentrations. The ratio of the intensity to concentration relative to that for 11.9 N is given in the third column. The fourth and fifth columns represent the corresponding values for the Raman line at λ 4567 A.U.

The Table contains two sets of measurements, one with the Raman line at λ 4226 A.U. excited by the mercury line λ 4046 A.U. and the other with the line at λ 4567 A.U. excited by the mercury line λ 4348 A.U. To see if there is any absorption in nitric acid, within the range of concentrations used in this experiment, the ratios of the intensities of the two lines for the different concentrations are given in column 6. This ratio is constant to within 4 per cent of the mean. This is well within the range of experimental error. Hence it can be concluded that there is no difference in absorption in the two regions of the spectrum for the different concentrations. It is found that with concentrations much higher than 11.9 N which is the highest in this set of measurements, absorption sets

TABLE I.

Concentration c	λ 4226 A.U.		λ 4567 A.U.		$\frac{I_{4226}}{I_{4567}}$
	Intensity I	$\frac{I/c}{I_{11.9}/11.9}$	Intensity I	$\frac{I/c}{I_{11.9}/11.9}$	
11.9 N	34.0	1.00	13.5	1.00	2.52
10.2 N	36.0	1.23	14.1	1.22	2.55
8.5 N	36.6	1.51	14.4	1.49	2.54
6.8 N	37.0	1.90	14.0	1.82	2.64
5.1 N	31.4	2.15	12.9	2.23	2.44
3.4 N	30.1	3.10	11.5	2.98	2.62
1.7 N	18.9	3.90	7.5	3.90	2.52
0.85 N	11.2	4.61	4.4	4.56	2.54
0.42 N	6.2	5.11	2.5	5.19	2.48

in due to the formation of slight quantities of nitrogen peroxide, in the shortest wavelength region and gradually increases at λ 4567 A.U. as well. Hence no attempt is made to extend the intensity measurements to still higher concentrations.

Now the intensity of each Raman line is proportional to the number of molecules or ions which give rise to it. If N_c is the number of free NO_3-ions and I_c the intensity of the Raman line due to them at concentration c, the degree of dissociation, which is given by the ratio of the dissociated to the total number of molecules, is given by

$$\alpha = \frac{N_c / c}{N_0 / c_0} = \frac{I_c / c}{I_0 / c_0}$$

where N_0 and I_0 correspond to infinite dilution when all molecules are supposed to be dissociated. Since it is not possible to determine the intensity of the Raman line at very large dilutions, the values of dissociation in Table I are given in terms of that at 11.9 N. The conspicuous increase of this value with diminishing concentration demonstrates the large increase of dissociation with dilution of the acid.

To compare these values of dissocation with those obtained from electrolytic conductivity measurements of nitric acid, the molecular conductivity data are given in Table II. The degree of dissociation, according to KOHLRAUSCH's formula, is given by

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

where Λ_c and Λ_0 are the molecular conductivities at concentrations c and 0 respectively. But a more accurate formula giving the dissociation is

$$a = \frac{\Lambda_c \, \eta_c}{\Lambda_0 \, \eta_0}$$

where η_c and η_0 are the viscosities of the solutions at concentrations c and 0. In Table II the values calculated from the viscosity formula alone are given.

In Table II, the first column contains the concentrations of nitric acid. The second and third columns represent the molecular conductivities and viscosities respectively at these concentrations. The values of dissociation calculated from the viscosity formula given above are represented in column 4. These are calculated in terms of the dissociation at 11.9 N, to make them comparable with those calculated from the intensity measurements. The latter sets of values are given in columns 5 and 6. The numbers in column 6 are the mean of the values in columns 3 and 5 of Table I.

TABLE II.

Concentration c	Λ in cm^{-1} ohm^{-1}	$\eta \times 10^4$ in g. cm^{-1} sec^{-1}	$\frac{\Lambda_c \eta_c}{\Lambda_{11.9} \eta_{11.9}}$	Concentration c	$\frac{I_c/c}{I_{11.9}/11.9}$
11.9 N	47.0	225.0	1.00	11.9 N	1.00
10.4 N	61.0	207.5	1.20	10.2 N	1.22
10.0 N	65.4	202.5	1.25	8.5 N	1.50
7.0 N	109.0	163.0	1.68	6.8 N	1.86
5.0 N	156.0	139.5	2.06	5.1 N	2.19
4.0 N	186.0	131.0	2.30	—	—
3.0 N	220.0	124.5	2.59	3.4 N	3.04
2.0 N	258.0	120.5	2.94	1.7 N	3.90
1.0 N	300.0	117.5	3.33	0.85 N	4.58
0.5 N	324.0	117.0	3.59	0.42 N	5.15
0.3 N	334.0	116.0	3.66	—	—

The curves showing the relation between concentration and dissociation from the two different methods given in columns 4 and 6 of the above table are graphically represented in Fig 3. The lower is from conductivity measurements and the upper from the intensity data of the Raman lines. It is evident from the curves that the dissociation found from the intensity measurements is higher at greater dilutions than that calculated from the conductivity data.

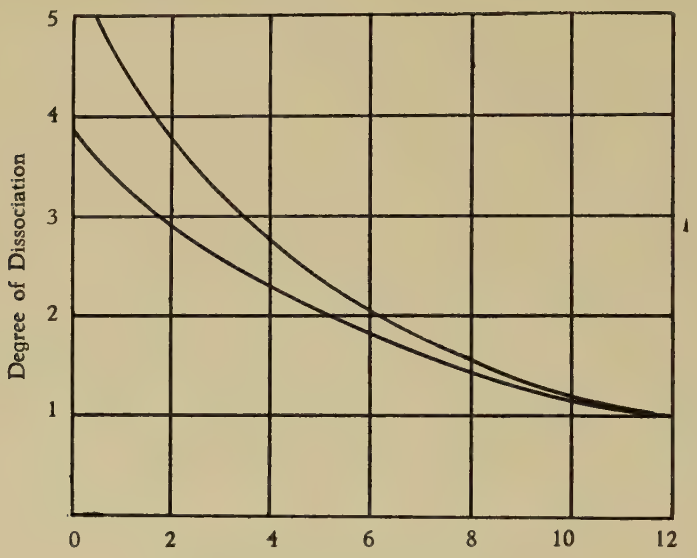


Fig. 3.

6. *Discussion.*

The above curves clearly show that the dissociation of nitric acid progressively increases with diminishing concentration. Even at such low concentrations as 0.42 N, which is the lowest attained in this work, the dissociation is still on the increase. This seems to support the view of progressive dissociation. Though the intensity measurements are not as accurate as those of electrolytic conductivity, the values of the degree of dissociation calculated from the former appear to be much higher than those calculated from the conductivity-viscosity formula. The difference is too much to be explained away as due to experimental error.

There are many factors which contribute to the uncertainty of conductivity-viscosity formula as giving the "true degree of dissociation", which is the ratio of the number of dissociated to the total number of molecules. The conductivity of an electrolyte is not a direct function of the concentration of the ions. It depends also on their mobility. The exact nature of the relation between mobility and viscosity is not definitely known. Hence the viscosity formula may not give the true degree of dissociation.

The intensity of the Raman lines, on the other hand, depends entirely on the number of ions, and is independent of either their concentration or mobility. Hence this method gives the actual proportion of the number of ions in the various concentrations, which no other method does.

It would have been possible to calculate the actual degree of dissociation by finding the intensities of the Raman lines at very high dilutions, where the dissociation is supposed to be complete. But on account of the very small intensity of these lines, it is not possible to determine with any accuracy the relative intensities. Hence the degree of dissociation relative to that corresponding to 11.9 N nitric acid only is calculated in this work. Further improvements in the excitation of Raman spectra may enable work with still further dilutions.

Before attempting to arrive at general conclusions regarding the nature of electrolytic dissociation from the measurements with the single electrolyte, nitric acid, further study with other substances is necessary. The author expects to do it in future.

7. *Summary.*

1. The Raman spectrum of nitric acid contains two strong lines, one of which is found also in nitrates. Study with different concentrations of nitric acid has shown that this line gets stronger in intensity with diminishing concentration, whereas the line that is present only in nitric acid but not in nitrates, diminishes in intensity.

2. This phenomenon is attributed to increasing electrolytic dissociation of nitric acid molecules with the formation of NO_3-ions on dilution.

3. An improved method of studying the actual amount of dissiciation, by measuring the intensity of the Raman lines, is described.

4. A comparison is made between the dissociation determined by the above measurements and that from electrolytic conductivity data. It is found that the former gives higher values of dissociation than the latter.

5. The difference is attributed to the uncertainty of the viscosity-conductivity formula as representing "the true degree of dissociation".

Part of the work done in King's College, London, had to be finished in Physisch Laboratorium, Utrecht, for accurate intensity measurements. The author is extremely grateful to Prof. O. W. RICHARDSON and Prof. L. S. ORNSTEIN for the facilities given in their Laboratories during the course of this work.

Physics. — *Analysis of the β Bands of Boron Monoxide.* By A. ELLIOTT, B.Sc., Fellow of the Rockefeller Foundation. (Communication from the Physical Institute of the University of Utrecht). (Communicated by Prof. L. S. ORNSTEIN).

(Communicated at the meeting of June 28, 1930).

Introduction.

It is the purpose of this communication to describe a new interpretation of the structure of two of the β bands of boron monoxide. While the measurements to be described are adequate for the determination of the structure, further measurements are necessary before the rotation constants can be accurately determined, and the values given for the latter will probably need revision.

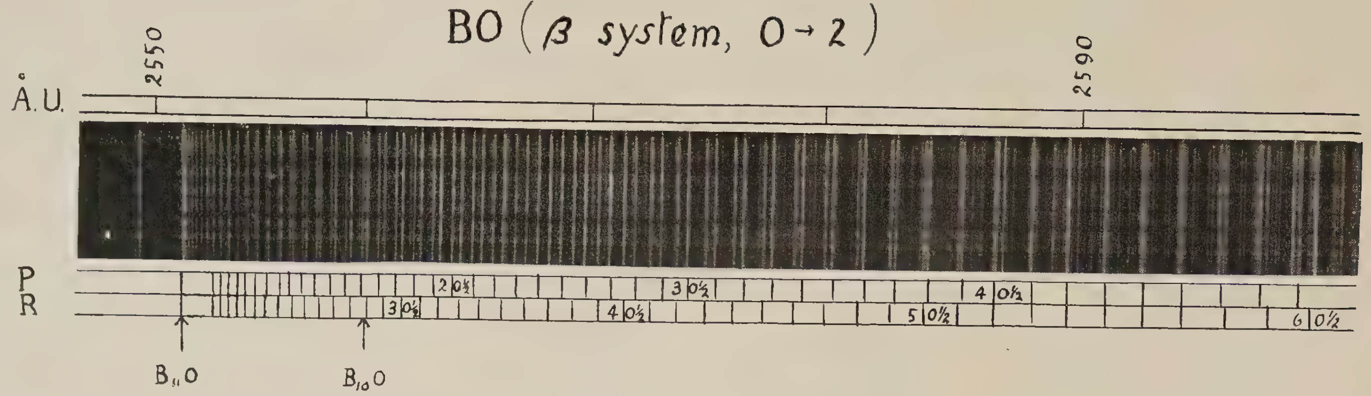
The bands of boron monoxide may be observed in an arc between carbons containing boric acid, and also in active nitrogen (containing a trace of oxygen), into which the vapour of boron trichloride is led. The latter source of the bands was discovered by Lord RAYLEIGH and the spectrum was measured and analysed by JEVONS (1), who attributed the spectrum to boron nitride on account of chemical evidence. The magnitude of the isotope effect points, however, as was shown by MULLIKEN (2), quite clearly to the monoxide of boron as the emitter of the spectrum.

Three electronic systems have been identified; the α system in the visible region ($^2\Pi \rightarrow {}^2\Sigma$), the β system in the ultra-violet ($^2\Sigma \rightarrow {}^2\Sigma$) and a weak intercombination system ($^2\Sigma \rightarrow {}^2\Pi$).

Some of the stronger α bands have been analysed by JENKINS (3), using the active nitrogen source, and more recently, SCHEIB (4) has analysed a number of the bands in the same system as they appear in the arc. Both investigators find the same structure; the different appearance of the spectra in the two sources is presumably in great measure due to the much higher temperature of the arc.

In the case of the β bands, however, important differences occur. MULLIKEN (loc. cit.) has pointed out that in these bands, in general, only one series of lines is to be observed in bands excited by active nitrogen, while two series of approximately equal intensity occur in the arc bands; one of the latter agrees in position with the single series of the former, and it was conjectured that this was an *R* branch. In a $^2\Sigma \rightarrow {}^2\Sigma$ transition, doublet *P* and *R* branches are to be expected, and MULLIKEN expressed the opinion that the second series of lines in the arc bands was not the missing *P* branch, but the other member of the

A. ELLIOTT: ANALYSIS OF THE β BANDS OF BORON MONOXIDE.



Proceedings Royal Acad. Amsterdam, Vol. XXXIII, 1930.

R branch doublet, which was not excited in active nitrogen. In the absence of other evidence, this seemed probable, but as will appear, it is almost certainly not the case.

Experimental.

During the course of an investigation on the intensity ratios of the isotopic bands in boron monoxide, the author was led to examine the β bands in the arc. A HILGER $E\,1$ quartz spectrograph was used to photograph the region 2400—2600 Å.U., where the dispersion is about 3 Å.U. per mm.; a reproduction of one of the bands in this region, taken with an exposure of four minutes, is shown in the figure. A narrow slit was used, and since no appreciable temperature shift could occur in the short exposure time, the maximum resolution was obtained.

The doublets in the bands of $B_{11}O$ mentioned by MULLIKEN (loc. cit.) were examined, and it was found that, at some distance from the head, each member of a doublet was itself double, the separation being, however, greater for the series of lines which appears also in bands excited by active nitrogen. The (fine) doublet separation increases with distance from the band head, and resolution begins at about the thirty-sixth and forty-fifth lines from the head in the wider and narrower series of doublets, respectively.

The frequencies of the lines in the $0 \rightarrow 1$ and $0 \rightarrow 2$ bands were measured, using iron arc lines as standards. In these measurements, the lines from the twentieth to the fiftieth from the head have been measured, and since the determination of the fine doublet separation was not the immediate object of the work, the mean frequency of these doublets has been determined. More complete measurements will be carried out later, and the results will be published in greater detail.

Analysis.

The appearance of the arc β bands described above is just what would be expected for a $^2\Sigma \rightarrow {}^2\Sigma$ transition with all the branches present. Bands of this type have a P and an R branch, each of them consisting of doublets whose separation increases linearly with the rotation quantum number; a consequence of the connection between these latter is that, when the R branch forms the head and the doublets become resolved after this branch has turned at the head, the R lines are resolved nearer the origin than the P lines. Since the two bands measured have a common initial level, identical combination differences of the type $R(j) - P(j) = \Delta_2 F'$, where j is the effective quantum number in the lowest electronic level, should be found if the two series of fine doublets are P and R branches (neglecting the fine doubling).

Two such sets of combination differences have in fact been found and are given in columns (2) and (3) of the table. The agreement is good enough the make it exceedingly probable that they are genuine

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Combination Differences.

	Upper State $\Delta_2 F'$		Lower State $\Delta_2 F''$	
	β bands		$0 \rightarrow 2$	
	$0 \rightarrow 1$	$0 \rightarrow 2$	β bands	α bands
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
27½			190.1	190.39
28½			196.7	197.26
29½	176.4	175.9	203.5	204.06
30½	182.0	181.5	210.8	210.65
31½	187.8	187.4	217.3	217.73
32½	193.8	193.0	224.1	224.58
33½	199.4	199.0	231.0	231.18
34½	205.2	204.9	237.7	237.73
35½	210.7	210.6	244.6	244.74
36½	216.9	216.6	251.6	251.50
37½	222.5	222.4	258.1	258.30
38½	228.1	227.8	264.9	265.11
39½	233.8	233.9	271.8	272.02
40½	239.6	239.7	278.5	279.37
41½	245.1	244.9	285.5	285.85
42½	251.5	250.3	291.9	292.38
43½	256.7	256.4		

$B' = 1.53$ cm^{-1}.

$\Delta_2 F'$ values. A further test can, however, be applied, since the α and β systems have a common final level, and the $\Delta_2 F''$ values must therefore be identical for bands which have the same vibrational quantum number in the final state in the two systems. For the β bands, the values of $\Delta_2 F'' = R(j-1) - P(j+1)$ can readily be calculated from the line frequencies after the $\Delta_2 F'$'s have been determined.

For the α bands, SCHEIB (loc. cit.) gives the same combination differences for the $0 \rightarrow 2$ and $0 \rightarrow 3$ bands from his analysis; in columns (4) and (5) of the table these differences for the $0 \rightarrow 2$ band in both systems are reproduced. The agreement is such that there can be no doubt that the $\Delta_2 F''$'s for the β band are genuine. We may therefore conclude without hesitation that the two series of fine doublets are P and R branches, and that the bands have the structure of $^2\Sigma \rightarrow {}^2\Sigma$ bands.

Rotation Constants.

Since the α and β systems have the same final level, the values of B'' are the same for both. The measurements of SCHEIB (loc. cit.) are more complete than those of the writer, and his values of B'' more accurate than any which could be calculated from the present results. Consequently, only the value of B' has been calculated.

SCHEIB gives as the connection between the effective quantum number and series number m in his tables

$$m^+ + {}^1/_2 = m \text{ (here } m^+ \text{ is the writer's } j)$$

but there seems to be a mistake in the sign in this formula, for on extrapolating his lower state term differences one finds

$$m^+ - {}^1/_2 = m$$

and the numbering derived from this result leads to the same B'' values as he gives; apparently therefore the correct quantum numbers have been used in calculating the constants. The constant B' has been calculated from the equation

$$\triangle_2 F'/j = 4B'.$$

This equation is only approximate, since $\triangle_2 F'$ is not exactly linear in j, and the value found in this way for B' varies over the range of $\triangle_2 F'$ values available from 1.492 at $j = 29^1/_2$ to 1.474 at $j = 43^1/_2$. The variation is approximately linear, and the best value for B' has been found by extrapolating to $j = 0$, since at this point the above equation holds. This value is given under the table.

Comparison of the bands in the arc and in active nitrogen.

From a comparison of the $0 \rightarrow 1$ band in the arc and in active nitrogen, it has been found that in the latter it is the P branch which is missing, as was suspected by MULLIKEN (loc. cit.). The latter found that in two bands excited in active nitrogen ($2 \rightarrow 0$ and $4 \rightarrow 1$) a weak second series of lines was present; this was presumably the missing P branch. Traces were also found in other bands, but in general only one branch was to be observed. It may be remarked here that the lines of this branch may be double as in the arc, but since the rotation structure in the active nitrogen source is not strongly developed, it is not to be expected that the doublets will be resolved with the spectrographs hitherto employed.

The fact that the transition $j - 1 \rightarrow j$, corresponding to the missing P branch, occurs in the arc and not in excitation with active nitrogen is very remarkable. It is possible that the strong fields present in the arc may be connected with the phenomenon. An investigation of the intensities of P and R branches under different conditions in the arc may perhaps throw some light on the problem.

In conclusion, the author wishes to express his thanks to Prof. ORNSTEIN for the facilities and help given him during the course of the work.

Summary.

The 0 → 1 and 0 → 2 bands of the β system of *BO* are analysed and doublet *P* and *R* branches are found. The combination differences for the excited state in these two bands agree with each other. It is also found that the normal combination differences for the 0 → 2 band agree with those given by SCHEIB (4) for the 0 → 2 band in the α system in *BO*.

A comparison of the β bands excited in the arc and in active nitrogen shows that, as was suggested by MULLIKEN (2), it is the *R* branch which is present in the latter case; the *P* branch is usually absent.

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Physiology. — *Experimentelle Untersuchungen über den Einfluss des Kohlenmonoxyd auf den peripheren Nerven.* Von F. KRAUSE, Düsseldorf. (Mitteilung aus dem Laboratorium der Neurologischen Klinik der Universität Amsterdam.) (Communicated by Prof. B. BROUWER.)

(Communicated at the meeting of June 28, 1930).

Erkrankungen der peripheren Nerven bei Kohlenmonoxyd Vergiftungen (im weiteren abgekürzt: CO-Vergiftung) gehören zu den Seltenheiten. Ueber die pathogenetische Entstehung dieser Erkrankungen sind mehrere Theorien aufgestellt worden, über die bisher jedoch keine einheitliche von allen Autoren acceptierte Auffassung erzielt werden konnte. H. CLAUDE (1), GÜNTHER (2), LITTEN (3), SCHWERIN (4), MANKOWSKY (5) u.a. sind der Ansicht, dass die Schädigung der peripheren Nerven auf mechanische Weise zu stande komme. Bei der CO-Vergiftung treten nach diesen Autoren häufig Blutungen in die Nervenscheiden oder ihre Umgebung ein und das secundär auftretende Hämatom alteriert auf mechanischem Wege die Nervenfasern; ein anderer Teil der auftretenden Schädigungen ist als Folge ischämischer Störungen oder mechanischer Kompression der Nerven anzusehen, die durch lange einwirkenden Druck oder abnorme Lage (Herabhängen der Gliedmassen u.s.w.) während der Bewusstlosigkeit bedingt sind. Die Auffassung, dass die peripheren Nerven secundär bei CO-Vergiftungen leiden, steht jedoch mit zahlreichen Beobachtungen der Klinik in Widerspruch. Häufig ist die Lokalisation bei der Nervenschädigung derart, dass dafür eine abnorme Lagerung der Erkrankten während der Bewusstlosigkeit ursächlich sicher nicht verantwortlich gemacht werden kann, so z.B. in den Fällen von SCHWABE (6): Neuritis des Opticus, von WILSON und WINKELMANN (7): Neuritis des Trochlearis, von KNAPP (8): Neuritis des Oculomotorius u.a. Weiter werden Blutungen in die Nervenscheiden oder in ihrer Umgebung bei Sektionen äusserst selten gefunden. In einem selbstbeobachteten Fall von schweren unmittelbar im Zustand der Vergiftung aufgetretenen typischen trophischen Hautveränderungen konnte ein derartiger Befund ebenfalls nicht erhoben werden.

Dieser rein mechanischen Auffassung wird daher von zahlreichen Autoren (BOURDON (9), LEUDET (10), WILSON u. WINKELMANN, u.a.m.) entgegengetreten. Von ihnen werden alle Erscheinungen (Muskellähmungen, Sensibilitätsstörungen, alle Abweichungen vasomotorischer und trophischer Art) auf eine durch das CO bedingte toxische Neuritis zurückgeführt. LAMIC (11), KOBERT (12), LEWIN (13) u.a. dagegen vertreten die Ansicht, dass die Erkrankung der peripheren Nerven in einer funktionellen Schädigung durch den Sauerstoff-Mangel ihre Ursache finde.

Diese Störung in der O_2 Versorgung kann in einem ungenügenden Angebot durch das Blut oder in einer Blokade der nervösen Substanz selbst durch Auftreten einer CO-Protoplasmaverbindung ihre Ursache finden. Auf diese Weise kommt es zu einer inneren Erstickung der Nerven. Diese Theorie wird eingehend von LEWIN begründet und vertreten.

Zusammenfassend haben wir also die folgenden drei hauptsächlichsten Erklärungsmöglichkeiten vor uns:

1. Es handelt sich um eine toxische Neuritis, wie wir sie vom Blei, Alkohol, usw. her kennen, oder
2. es liegt vor eine Schädigung des Nerven vorwiegend durch mechanische Momente verschiedener Art, oder
3. das CO verhindert einen für die Funktion genügenden O_2 Transport zum Protoplasma des Nerven.

Die Lösung dieser Frage wurde auf experimentellem Wege weiter noch nicht angegangen. Wohl liegen Versuche von FEDERICI (14), MEYER (15) u.a.m. vor, die Tiere mit CO akut und chronisch vergifteten. Von diesen Autoren wurden allerdings vorwiegend die Veränderungen im Centralnervensystem untersucht. Nur FEDERICI geht in seiner Arbeit kurz auf die gefundenen Veränderungen des peripheren Nerven ein und erwähnt, dass sie den durch andere Vergiftungen hervorgerufenen gleichen und nichts für die CO Vergiftung Charakteristisches aufweisen.

Das Ziel dieser Arbeit ist nun, dadurch zur Klärung dieser Frage einen Beitrag zu liefern, dass wir die Funktion des peripheren Nerven unter dem Einflusz von Kohlenmonoxyd untersuchten. Dabei haben wir uns von folgenden Ueberlegungen leiten lassen.

Wie oben bereits kurz auseinandergesetzt, stützt sich eine Theorie der peripheren CO Lähmungen auf die Annahme, dass die Schädigung des Nerven durch die Beschränkung seiner Atmung hervorgerufen wird. Diese Behinderung in seinem Sauerstoffbedarf kann dadurch zustande kommen, dass sich das Hämoglobin mit dem CO bindet und dadurch nicht mehr in genügendem Masse als Sauerstofftransportmittel in Betracht kommt. Diese Vorstellung dürfte kaum zutreffend sein; denn aus der experimentellen Physiologie ist es zur Genüge bekannt, mit wie wenig Sauerstoff das periphere nervöse Gewebe seine Funktion aufrecht erhalten kann. Bevor also bei der CO Vergiftung das periphere Nervengewebe durch den Sauerstoffmangel so leidet, dass es geschädigt wird, werden sicher bereits andere Organe (Herz, Niere), die in ihrer Funktion viel stärker von der Sauerstoffzufuhr abhängig sind, so schwer alteriert, dass der Tod eintritt. Um diesem Einwand zu begegnen hat man gesagt, das CO geht mit dem Protoplasma des Nerven eine CO-Protoplasmaverbindung ein, ähnlich, wie es auch das Hämoglobin tut, und auf diese Weise kommt die Erstickung des Nerven zustande, die dann zur anhaltenden, funktionellen und später auch anatomischen Schädigung führt. Um diese Frage näher zu prüfen, haben wir den Einfluss des Leuchtgases auf die Funktion des peripheren Nerven untersucht, wobei wir als Masstab der Funktion das

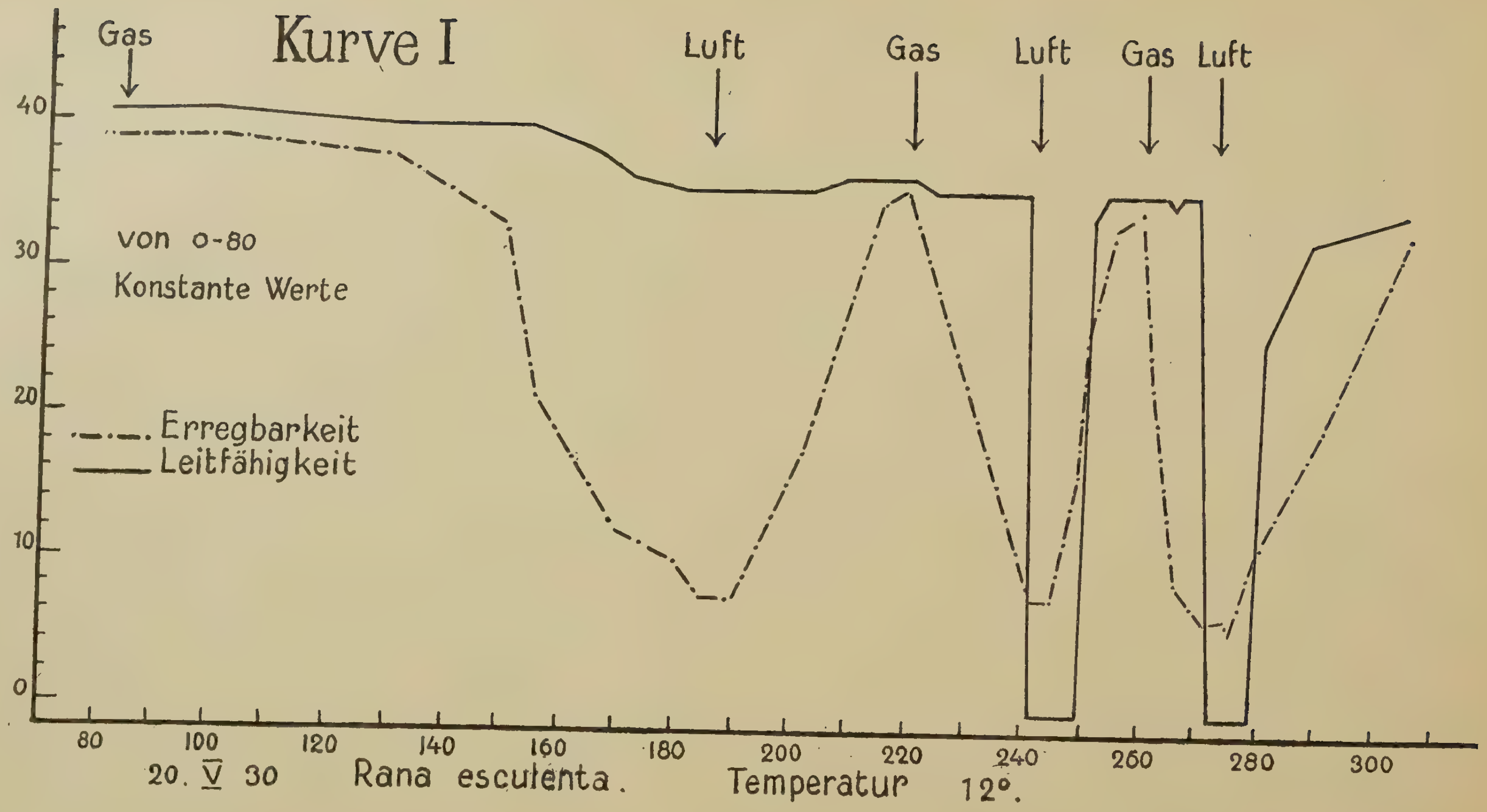
Verhalten des Nerven gegen den elektrischen Strom (Leitfähigkeit und Erregbarkeit) benutzten.

Die Versuchsanordnung wurde so gewählt, wie sie bei den Untersuchungen verschiedener gasförmiger Stoffe auf die Erregbarkeit und Leitfähigkeit des Nerven üblich ist. Der Nerv eines Nervmuskelpräparates vom Frosch kommt auf eine kurze Strecke in eine Glaskammer und wird hierin der Einwirkung des CO ausgesetzt. In dem Stück des Nerven, der sich in der Kammer befindet, wird die Erregbarkeit und distalwärts vom Muskel ausserhalb der Kammer die Leitfähigkeit des Nerven geprüft. Die Stärke der in und oberhalb der Kammer zur Erregung nötigen Schwellenreize wurden im cm. Rollenabstand ausgedrückt und als Ordinaten in ein Koordinatensystem eingezeichnet, auf dessen Abscisse die Zeiteinheiten eingetragen werden. Die auf diese Weise erhaltenen Kurven illustrieren das Verhalten der Erregbarkeit und Leitfähigkeit des peripheren Nerven unter dem Einfluss von CO. Die Werte der Leitfähigkeit in den Kurven sind dabei naturgemäss nur ein Masstab für die Veränderung, die die Leitfähigkeit im beeinflussten Nervenstück erfährt, und nicht als absolute Zahlen anzusehen. Unter dem Begriff der Leitfähigkeit ist also zu verstehen, das Durchlaufen der Erregungswelle durch die veränderte Nervenstrecke. Die Prüfung dieses Verhaltens wird allgemein als Funktion der Leitfähigkeit registriert. Der gedankliche Fehler bei dieser Unterstellung soll im weiteren Teil der Arbeit nicht mehr berücksichtigt werden.

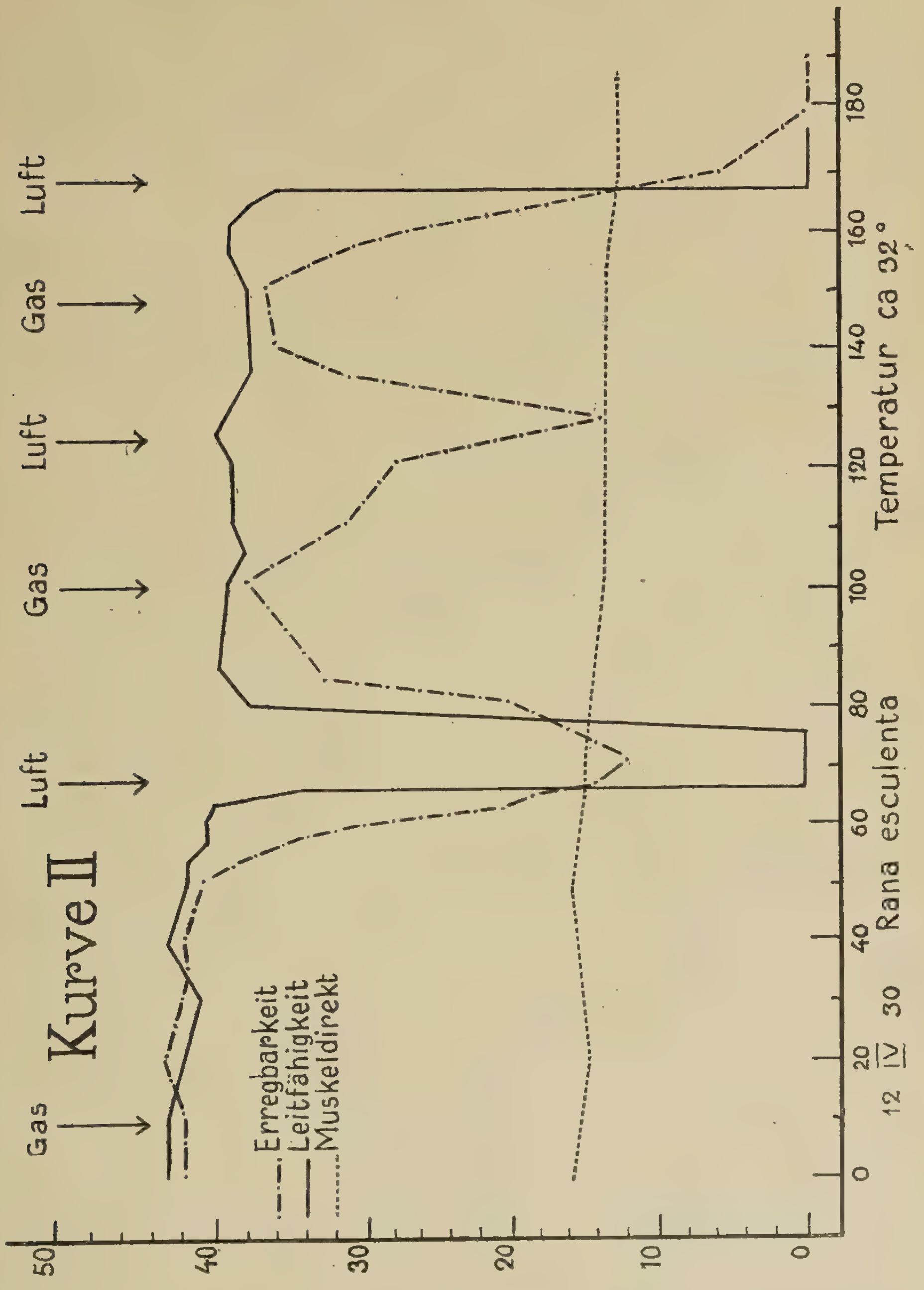
Zur Reizung wurde ein einfaches Schlitteninduktorium verwandt und als Stromquelle diente ein Chromsäureelement. Das Gas wurde unmittelbar der Leitung entnommen, passierte mehrere Waschflaschen, damit es auf eine gewünschte Temperatur gebracht wurde, und wurde nach dem Durchstreichen durch die Glaskammer ins Freie geleitet. Die Versuche wurden durchgeführt an Esculenten in den Monaten März — Mei.

Von den 18 gelungenen Versuchen sollen einige typische Kurven hier wiedergegeben werden:

Der Versuch, Kurve I, wurde bei einer Temperatur von 12° ausgeführt. Die Erregbarkeit beginnt etwa nach 140' zu sinken und nach etwa 180' ist sie auf einen Rollenabstand von ca. 8 cm. gefallen. Die Leitfähigkeit ist in der gleichen Zeit nur von einem Beginnwert 42 cm. auf etwa 36 cm. abgesunken, hat also praktisch genommen ihre Anfangshöhe behalten. Ein so geringer Abfall ist durch die lange Dauer des Versuches erklärt. Zu diesem Zeitpunkt wird die Gaszufuhr unterbrochen und Luft eingeleitet. In kurzer Zeit steigt die Erregbarkeit wieder auf 38 cm. Erneute Leuchtgaszufuhr lässt die Erregbarkeit schneller fallen und bei einem Wert von etwa 10 cm. Rollenabstand sinkt die Leitfähigkeit plötzlich auf Null. Durch sofortige Luftzufuhr erholen sich sowohl die Leitfähigkeit wie auch die Erregbarkeit schnell und zwar steigt die Leitfähigkeit nach etwa 10' plötzlich auf ihren Ausgangswert, während die Erregbarkeit in Stufen ihre alte Höhe erreicht. Das Experiment lässt sich nochmals in gleicher Weise reproducieren.


Kurve I
Gas
Luft
Gas
Luft
Gas
Luft
von o-80
Konstante Werte
Erregbarkeit
Leitfähigkeit
40
30
20
10
0
80
100
120
140
160
180
200
220
240
260
280
300
20. V 30
Rana esculenta.
Temperatur 12°.

Ein weiterer Versuch wurde angestellt bei 32° und ist wiedergegeben in Abbildung II. In diesem Falle ist noch eine dritte Ordinate in die



Figur eingezeichnet, die zum Vergleich die direkte Erregbarkeit des Muskels in cm. Rollenabstand angibt. Man könnte sonst den Einwand erheben, das CO, das sich naturgemäss auch immer in kleinen Konzentrationen ausserhalb der Kammer befindet, schädet die Substanz des Muskels und verhindert dadurch, dass ein noch wirksamer Reiz des Nerven einen Effekt am Muskel zeitigt. Bei einigen einleitenden Versuchen, in denen die seitlichen Oeffnungen der Glaskammer nicht sorgfältig genug abgedichtet waren, zeigte sich in der Tat eine Lähmung des Muskels, die sich selbst bei langer Luftzufuhr als irreversibel erwies.

Im übrigen zeigen die Kurven in der 2. Abb. das gleiche Verhalten wie in Abb. I. Der Erfolg der CO. Einleitung tritt allerdings hier bereits früher ein, etwa nach 60′. Das ist zurückzuführen auf die wesentlich höhere Temperatur, bei der dieser Versuch durchgeführt wurde. Auch aus den anderen Experimenten haben wir den Eindruck gewonnen, dass die Geschwindigkeit des Eintretens der elektrischen Veränderungen mit steigender Temperatur zunimmt. Am Ende dieses Versuches erholt sich die Funktion der Erregbarkeit und Leitfähigkeit nicht mehr, während die direkte Erregbarkeit des Muskels annähernd während der gesamten Versuchsdauer unverändert bleibt.

Es liess sich also ein gleiches Verhalten der Erregbarkeit und Leitfähigkeit des Nerven bei Zufuhr von Kohlenmonoxyd nachweisen, wie es von v. FRÖHLICH (16), GRÜNHAGEN (17), HOPKINS (18), KATO (19), KOCH (20), u. a. m. für Stickstoff und verschiedene gasförmige Narkotica bereits gezeigt war. Die Erregbarkeit in der Kammer sinkt zunächst langsam ab. In diesem Stadium hat der Nerv an der Stelle, wo seine Leitfähigkeit geprüft wird, noch seine volle Erregbarkeit. Sinkt die Erregbarkeit weiter, so kommt plötzlich ein Punkt, wo die Leitfähigkeit auf Null sinkt d. h. von oberhalb der Kammer ist keine Muskelkontraktion mehr zu erzielen. Auf die theoretische Erklärung dieser Dissociation von Erregbarkeit und Leitfähigkeit, die schon häufig Gegenstand lebhafter Diskussion gewesen ist und in neuerer Zeit durch die Arbeiten von KATO, HOPKINS, KOCH, endgültig geschlossen wurde, soll hier nicht näher eingegangen werden. Der springende Punkt bei unseren Untersuchungen liegt in dem zweiten ansteigenden Schenkel der Kurve, in der Erholungsphase. Wurde zeitig genug Luft zugeführt, so erlangen die Werte der Erregbarkeit und Leitfähigkeit des Nerven schnell ihre alte Höhe; wenn die Gaszufur nach Erlöschen der Leitfähigkeit noch eine Zeitlang fortgesetzt wurde, so erwies sich der Nerv als irreparabel in seiner Funktion geschädigt. Beide Befunde sind charakteristisch für das Verhalten des Nerven in der Erholungsphase, die aus den Erstickungs- und Narkoseversuchen am Nerven lange bekannt sind.

Aus unseren Experimenten können wir also den Schluss ziehen, dass eine feste chemische Bindung des CO an das Protoplasma des Nerven nicht stattfindet. Wenn das der Fall gewesen wäre, könnten wir nicht erwarten, dass die Erholung des Nerven in dieser Weise vor sich ginge. Der Zerfall einer derartigen Verbindung geht, wie vom CO Hämoglobin her bekannt ist, bei Anwesenheit von Luft nur sehr langsam vor sich.

Der Einfluss des CO ist demnach derselbe wie der eines indifferenten

Gases z.B. Stickstoff und beruht nur darauf, dass der Nerv in seiner Sauerstoffaufnahme durch Drosselung der Sauerstoffzufuhr gehindert wird.

Kehren wir jetzt zu unserer aus der Klinik abgeleiteten Fragestellung zurück, so kann die Erklärung der Entstehung der peripheren nervösen Erkrankungen durch die Annahme, dass das CO sich mit dem Protoplasma des Nerven chemisch bindet, nach dem Ausfall unserer Experimente als widerlegt gelten.

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Botany. — *Ueber das Entstehen von Zygophoren von Mucor Mucedo (+) unter Beeinflüssung eines von Mucor Mucedo (—) abgeschiedenen Stoffes.* Von C. VERKAIK. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated at the meeting of June 28, 1930).

Die vorliegende Untersuchung soll einige experimentelle Daten geben, aus denen hervorgeht, dass die von BURGEFF in seiner interessanten Arbeit (Botan. Abhandlungen Heft 4, 1924) ausgesprochene Meinung, es würde das Entstehen von Zygophoren von Mucor Mucedo (+) bei Anwesenheit von Mucor Mucedo (—) mittels telemorphotischer Wirkung hervorgerufen, nicht genügend durch die Tatsachen gestützt ist.

Nach einer experimentellen Voruntersuchung mit derselben Rasse von Mucor mucedo, welche auch BURGEFF benutzte und die in dankenswerter Weise vom „Centraal Schimmelbureau" in Baarn bezogen werden konnte, war es möglich mit nachstehenden Experimenten den Beweis zu bringen, dass die Zygophoren von Mucor Mucedo (+) unter Beeinflüssung durch einen Stoff, welcher von einem Mucor Mucedo (—) Mycelium abgeschieden wird, entstehen.

Die Kulturen wurden auf einem Nährboden von folgender Zusammensetzung gezüchtet:

250 gr.	Malzextrakt
750 gr.	destilliertes Wasser
20 gr.	Agar-agar
6 c.c.	KOH.1n

Andere Nährböden haben sich als unzureichend erwiesen. Auch muss man sehr darauf achten, dass die Kulturen nicht austrocknen, weil dies öfters zu Missbildungen führt.

Um die zu benutzenden Mycelia von einander isolieren zu können und doch eventuell abgeschiedene Stoffe aufzufangen, werden Celloidinplättchen benutzt, welche nach vielen Fehlversuchen auf die nachstehende Weise angefertigt worden sind. Man giesst eine 10 % Celloidinlösung auf eine sorgfältig gereinigte Glasplatte (80 × 30 × 1 mm.). Das überflüssige Celloidin lässt man abtropfen, und gleich darauf legt man die Glasplatte etwa 40 Sec. horizontal. Dann wird die Platte 60 Sec. in 80 % Alkohol und darauf ca. 60 Sec. in destilliertes Wasser gebracht. Zum Schluss kann man mit einem Rasiermesser die Celloidinplatte bequem von der Glasplatte abheben.

Es wurde dann weiter so verfahren:

Auf die peripheren Teile einer Kultur von Mucor Mucedo (—) (siehe Fig. 1 a Längsschnitt und b Querschnitt), welche sich in einer Petrischale (4) entwickelt, wird ein Celloidinplättchen (3) (25 × 75 × 0.5 mM.) in der Weise gelegt, dass ein Drittel der Oberfläche des Plättchens auf der Kultur liegt, zwei Drittel aber auf dem noch unbewachsenen Agarboden. Hierauf bringt man dann ein zweites kleineres Plättchen (2) (16 × 8 × 0.5 mM.) und sodann wieder eine Platte (3), welche die gleichen Abmessungen wie das 1e Plättchen hat. Auf diese 3 Plättchen, von welchen das 2e also an allen Seiten von den zwei anderen begrenzt, und von der Umgebung isoliert ist, bringt man nun ein Stückchen Agar-agar (1) (5 × 10 × 10 mm.), das aus einer Kultur von Mucor Mucedo (+) genommen ist, welche ein Alter von 2 Tagen hat. Das Agarstückchen wird umgekehrt auf die Celloidinplättchen gelegt, derart, dass das Mucor Mucedo (+) Mycelium mit dem Celloidin in Kontakt steht.

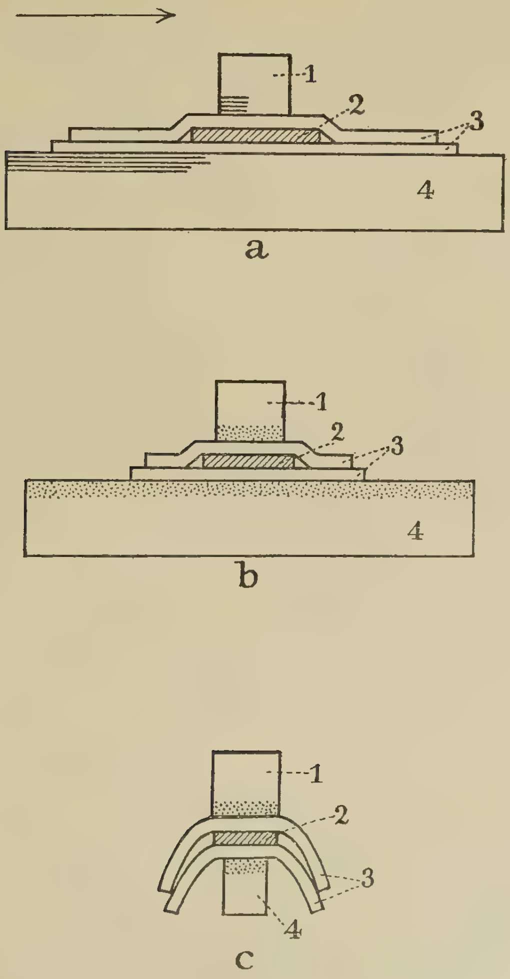

Fig. 1.

Nach zwei Tagen werden auf der oberen Celloidinplatte und auf den aufgebrachten Agarstückchen Zygophoren gefunden. Das kleine, mittlere, an allen Seiten von der grossen Platten umgebene Celloidinplättchen wird nun isoliert in eine steriele Petrischale mit Agar gelegt und hierauf ein neues Agarstückchen mit einem Mycelium von Mucor Mucedo (+) gesetzt. Nach weiteren zwei Tagen zeigten 2 von den 10 benutzten Petrischalen Zygophorenbildung. Weil wahrscheinlich das Mycelium der Mucor Mucedo (—) Kultur zwischen die 2 grossen Celloidinplatten gewachsen war, zeigten die anderen 8 Schalen Zygosporenbildung. Um die Nachteile. welche die möglichen Infektionen mit sich bringen, aufzuheben, kann der Versuch auf folgende Weise noch exakter gemacht werden. (Siehe Fig. 1c Querschnitt.)

In eine sterile Petrischale wird ein Stück Agar (4) von nur 6 × 80 × 10 mm. gebracht, welches einer 2 Tage alten Kultur von Mucor Mucedo (—) entnommen ist. Hierauf setzt man nun die 3 Celloidinplatten (2 und 3) und das Stückchen Agar (1) mit Mucor Mucedo (+), wie bei der ursprünglichen Anordnung. Da die 2 äusseren Celloidinplättchen viel grösser als das untere Stück Agar mit dem (—) Mycelium sind, so biegen sie sich infolge ihrer Schwere an den Seiten nach unten. (Siehe Fig. 1c.) Auf diese Weise ist Infektion des mittleren Celloidinplättchens vollkommen ausgeschlossen.

Später wurde dann das mittlere Celloidinplättchen genau so wie bei der früheren Versuchsreihe in eine andere Petrischale mit frischem sterilem Agar gebracht. Von den 10 so gemachten Versuchen, gaben 7 Versuche ein positives Resultat; 5 Versuche zeigten viele, 2 wenige Zygophoren. Eine Schale war infiziert; in 2 Schalen wurden keine Zygophoren gebildet. Eine von solchen Petrischalen gemachte Photographie zeigt die stark chemotropisch gekrümmten Zygophoren. (Siehe Fig. 2.)

Diese Versuche haben somit wohl den Beweis erbracht, dass ein Stoff, welcher von den Mucor Mucedo (—) zu den Mucor Mucedo (+) Kulturen diffundiert, als Ursache der Zygophorenbildung anzusehen ist, weil das kleine Celloidinplättchen, welches niemals mit einer Mucor Mucedo (—) Kultur in Kontakt gewesen ist, dennoch Zygophorenbildung einer Mucor Mucedo (+) Kultur hervorruft.

Botanisches Laboratorium.

Utrecht, Juni 1930.

C. VERKAIK: UEBER DAS ENTSTEHEN VON ZYGOPHOREN VON MUCOR MUCEDO (+) UNTER BEEINFLÜSSUNG EINES VON MUCOR MUCEDO (—) ABGESCHIEDENEN STOFFES.

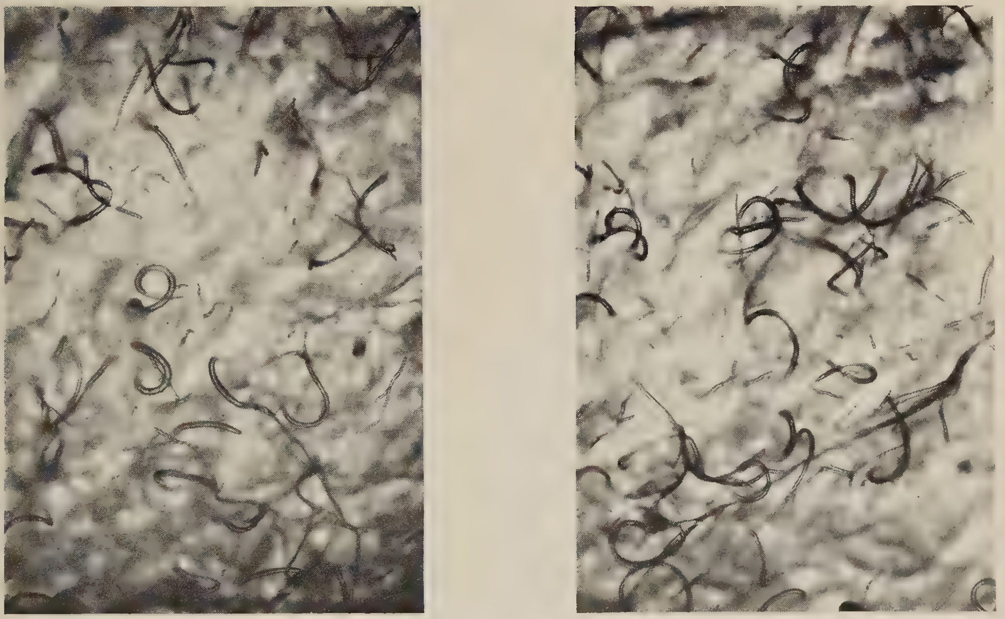

Fig. 2.

Anthropology. — *Investigation of blood groups in Holland.* I. By M. A. v. HERWERDEN and TH. J. BOELE-NIJLAND. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of June 28, 1930).

The biochemical section of the Anthropological Commission nominated by the Royal Academy of Sciences started to work in the summer of 1926. This section investigates the distribution of blood groups in the population of The Netherlands and its relation to other anthropological traits.

It is to be regretted, that Prof. BOLK, who initiated the Anthropological Commission of the Royal Academy, and who always was particularly interested in the work of our section, died before the results could be communicated by him in this meeting.

We first intended to have physicians all over the country participate in this research. Haemotest had to be furnished from a central point and the agglutination had to be undertaken according to our indication, by the physicians in different local districts. Thanks to the cooperation of the State Serological Institute at Utrecht the right treatment of the serum had been ascertained, which we were able to test before use. However — it soon became evident that the reaction of haemagglutination, simple though it may seem to be, demands the utmost care and experience. This can only be attained if all the agglutination tests are accomplished in a central place by one or two persons with sufficient routine. It is only in this way that one may avoid possible errors with pseudo- and auto-agglutination and so on. Moreover it can not be expected from the physicians, taken up by their practice, to give full attention to the minute details of these reactions. With some rare exceptions which will be mentioned in later papers, all the agglutinations during these 4 years have been done centrally in our laboratory at Utrecht University.

The Technique.

One or two drops of blood are collected in small tubes filled with ± 0.5 cc of a solution of 1 procent sodium citrate in 0.85 procent of sodium chlorate. To this mixture 0.1 procent superol has been added in order to avoid infection. The corked tubes are placed in boxes divided in numbered parts. So every blood specimen bears its own number, corresponding with the numbers of an accompanying list, on which several data relating to the persons in question are filed.

The blood proofs have been tested after the method of HIRSZFELD[1]) and LATTES[2]), that is to say on slides. This technique can only be used, if care is taken that the quantity of the blood suspension added to the drop of haemotest, is very small.

The blood suspension having been sufficiently diluted, a very tiny drop of the suspension is added to a much larger drop of haemotest. Without exception every test has been repeated a second time. In order not to overlook a retarded agglutination, each row of slides has been inspected twice or thrice. For observing agglutination a loupe (magnification × 10) has been used. Cases suspected of pseudo-agglutination have been rejected. As our experience increased, hesitation as to pseudo- or real agglutination disappeared. Only in testing the blood from the umbilical cord, which with a special aim had been sent to us by a cooperator, we could not always exclude the possibility of pseudo-agglutination.

In the latter years some authors advocated testing the blood in small tubes instead of using slides. We compared both methods without getting a better result with tubes. For practical reasons the use of tubes for the double agglutination proof has many disadvantages in anthropological research. It sometimes occurred that 200 determinations had to be done in a day, which means 600 tubes to be cleaned instead of the 200 containing the blood specimen. If one only takes care to use a sufficient large drop of haemotest in order to avoid evaporation before the reaction sets in, and to take the drop of blood suspension sufficiently small, mixing it well with the serum, the reaction appears soon and conspicuously. In a doubtful case one always can put the slide in a moist chamber for some time. For anthropological purposes it is sufficient to test only the erythrocytes of a person, without testing also his serum on agglutination. Only in juridical cases (examination for parenthood e.g.) we always examined the serum as well as the blood corpuscules, before stating the blood group of a person.

When the blood had to be collected in other communities, boxes with numbered tubes, filled with the above named solution, have been sent to the collaborator (physician or medical student) and were returned within 24 hours after the collecting of the blood drops. Though apparently it is still possible to test the blood group after some weeks, we never departed from the principle to investigate as early as possible. After some weeks the strength of the reaction diminishes even in the sterile solution.

The haemotest came from different sources, furnished regularly by some clinical colleagues. It was not easy to get haemotest in sufficient quantity. We even have been sometimes obliged to ask haemotest *B* from Deli, where Dr. VERHOEF, one of the pioneers on the field of blood group investigation, was able to procure a very active specimen. After sterile filtration the serum was put in ampullae of 1 cc by the State Serological Institute and tested in our laboratory. In the two last years the duplicate determinations always have been made for control with two haemotests from different origin.

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[1]) Konstitutionsserologie und Blutgruppenforschung. Verlag JULIUS SPRINGER 1928.

[2]) L'individualité du Sang. MASSON et Cie. Paris 1929.

From time to time the titer of the serum has been tested. The results of the agglutination proofs have been noted independently of the other anthropological data and added to the list afterwards.

For a review of the reaction of haemagglutination, we refer to the litterature on this subject, especially that collected in the publications of HIRSZFELD 1) and LATTES 2). The four blood groups in man are respectively called *O*, *A*, *B* and *AB*. When using serum from persons belonging to group *A* and *B* as haemotest, it is possible to discern the four different groups. After the current opinion the socalled agglutinines of the serum are bound by the agglutinogenes of the red blood corpuscule, causing the process of agglutination. In the scheme fig. 1 the way of reaction is indicated. Though the investigations of LANDSTEINER and others have demonstrated that subgroups in man doubtlessly exist, these researches are not ripe for practical use.

	Serum:	O	A	B	AB
Erythrocytes:	O	—	—	—	—
	A	+	—	+	—
	B	+	+	—	—
	AB	+	+	+	—

Fig. 1.
Scheme of agglutination test.

During our investigation we had the opportunity in special cases to test the hereditary foundation of haemagglutination. As an example we reproduce a pedigree studied by one of us, showing the offsprings of a marriage *A* × *B* (fig. 2).

In several pedigrees spreading over some generations in our country, one only finds the frequent group *O* and *A*. One of our students belonging to group *O*, proved to have ten brothers and sisters of the same group. As might be expected both the parents belong to group *O*. Another case reproduced here (fig. 3) responds to the theory of BERNSTEIN, after which *AB* does not genotypically include the factor *O*, as is the case with group *A* and *B*. In a marriage of a man *O* with a woman *AB*, none of the 14 children belonged to group O. In this family two identical twins, as might be expected, belonged to the same blood group (*B*). All the remaining

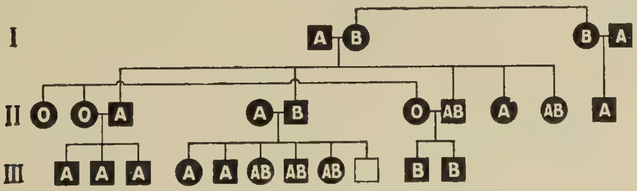

Fig. 2. Bloodgroups in three generations.

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1) l.c.
2) l.c.

children born before and after the twins, had inherited the *A* factor from the mother *AB*. A large pedigree comprising several generations, collected with the aid of two students in a rural district, will be given in another publication.

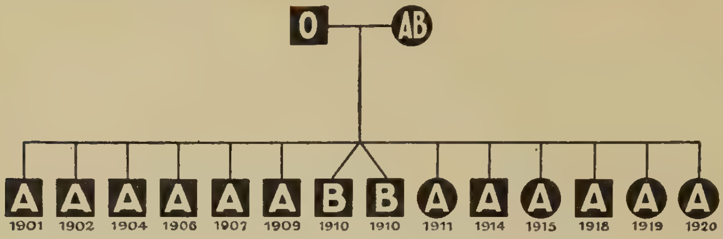

Fig. 3. The blood group relation in a family with 14 children.

Neither qualitatively nor quantitatively homozygotes *AA* and *BB* could be distinguished from heterozygotes *AO* and *BO*. In cases where control has been possible (e.g. with children from a marriage *A* × *O* or *B* × *O*), we never succeeded in stating any difference. In group *AB* frequently (not always) agglutination proves to be more intensive with the *A* haemotest than with the *B* haemotest. The same observation has since been published by O. THOMSEN [1]) in Copenhague.

When our section started work, there only existed 200 "Dutch cases" in foreign litterature — thanks to some blood specimen sent from Amsterdam to Professor L. H. SNIJDER at North Carolina University U. A. and tested there. Since investigators are interested in the distribution of blood groups in different races, an inventory has been made frequently. So these 200 inhabitants of Amsterdam have been used during many years for the statement of the blood group relation in the Netherlands. One readily understands that, on account of the small number as well as on account of the local origin, these cases are not able to give any idea of the blood groups in the Dutch population. In the wellknown book of HIRSZFELD [2]) the percentages which one of us has communicated as the preliminary result of our investigations, on occasion of the Congress of the "Institut International d' Anthropologie" at Amsterdam in 1927 [3]), are mentioned. These figures have since been copied by other authors; sometimes erroneously.

The remarkable researches of Mr. and Mrs. HIRSZFELD [4]) suddenly draw attention to the anthropological signification of the blood groups. They gave the instigation to Professor L. BOLK, president of the Dutch

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[1]) Ukrainisches Zentralblatt f. Blutgruppenforschung. Bd. 3 H. 2. 1929, p. 103. Zeitschr. f. Rassenphysiologie Bd. 1, 1929 p. 198.

[2]) l.c.

[3]) In our preliminary publication we avoided to calculate percentages from small numbers as has been done in the reproduction of our table in HIRSZFELD's book p. 111.

[4]) The Lancet, Vol. 180, p. 678, 1919.

Anthropological Commission to add a biochemical section for the study of the blood groups in the Netherland population.

Soon afterwards in Germany a blood group investigation with anthropological purposes has been started on large scale, conducted by O. RECHE and P. STEFFAN. In that country a principle has been followed, which we meant to avoid. In Germany namely, haemagglutination has been trusted to the physician practizing in rural districts, a central office supplying the haemotest. Holland, among some other countries, has been invited to join. We thought it better to refuse, on account of the above-named reason. Moreover the plans for a Dutch independent investigation lay ready at that time.

From all the persons, tested for their blood group, some other anthropological traits are noted. Besides the name, sex, data of birth, for every person the hair- and eye-colour, the shape of the head (in a number of cases accurate determinations of the head-index and the body-length[1])) are added. Further the birth place and place of residence, the origin of parents, grandparents and forefathers, eventual jewish and foreign origin. To the shape of the head by rough estimation, though mentioned in several cards, we only exceptionally attribute any value. For the examined students mentioned in this publication, the head dimensions have been measured by well-instructed assistents. This is also the case with more than thousand persons investigated by a collaborator in the "Hoeksche Waard" (province of Z. Holland), an adequate number on the "Veluwe" (province of Gelderland) and a lesser number in the province of Zeeland. In a later publication these investigations will be dealt of in detail.

For every person a personal card has been arranged, giving opportunity to make ample use of the collection, also for further investigation. The description of anthropological traits besides the blood group, opens the possibility to trace eventual correlation with this latter one — a subject still open to discussion in the litterature.

The investigations continued during ± 4 years, relate to ± 30000 persons selected in different ways. The results as a whole will be treated of in later publications, a part of them by collegues collaborating with us. *Only the data relating to the examination of a large number of students in Dutch universities have been till now elaborated in details,* those of the local investigations being still unfinished. In several places the numbers prove to be insufficient. It is not so easy to persuade people in Holland to furnish a drop of blood, as it is in more eastern or southern countries. In some rural places religious prejudices prevent the collection of the blood, in other localities one encounters an unexplained resistance. In this last year the influence of the discussion in the press about the vaccination problem has

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1) The body length, though not yet taken into account in this paper, has been noted for the greater part of the students taken up in our investigation. We prefer to postpone the shifting of the figures relating to this subject, untill all the data about the students have been transported on personal cards, which will be accomplished ere long.

been distinctly felt: many parents of schoolchildren in the country considered our investigation to be a concealed vaccination and refused their consent. Moreover there are several districts where it proved to be impossible to obtain any cooperation of the local physician. It is difficult to say whether this has been due to a lack of scientific interest, real lack of time or to resistance of the population. The fact remains that sometimes in districts which the local physician considered as inaccessible, our medical students were able to collect a large number of cases. If the population had proved less resistant, if many doctors in the rural districts had shown more perseverance after their initial promise of cooperation, if in general our young medical doctors were more interested in a scientific problem, which touches medical practice — more result would have been obtained with less labour. However the enthousiastic help of our students and the steady assistance of some of our colleagues have given compensation. Two of these collaborators will take their doctor degree on this subject relating to a special field of work.

The Investigation of 3085 Students.

This selected group of young people have their origin in different parts of the country. There are few near relations amongst them, which is always difficult to avoid in the local investigations. In a later paper we will discuss the part played by local intermarriage on the distribution of the blood groups in the Netherlands. For the group represented by the students, this question remains out of consideration. The students represent more or less a special group in society, though not at all in the way they did some scores of years before. It can be said that actually amongst the students of medicine, of dentistry, of biology and chemistry, of technical science (who especially were used for this investigation) different social layers are represented. Only the upper and the lower stratum of society is lacking in this material [1]). Besides the blood group, hair- and eye-colour and index cephalicus have been investigated in these 3085 students [2]); for a part also the body length. Moreover the origin of the grandparents on both sides has been noted and the eventual foreign (also jewish) origin, when these data were obtainable.

The greatest number of students have been investigated at Utrecht and at Delft University. This has the advantage that in both of these universities students resort from the greater part of the country. It is true that in Utrecht University the southern and middle part of the country are more represented than the northern part. Still also many Frisians or students of Frisian descent are found amongst them.

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[1]) No permission has been obtained by our commission from the War-Office to test the blood group of the conscripts.

[2]) Since our calculations have been finished, the number of students investigated has grown to 3191. All the students described in this paper are of Netherland nationality.

			HEAD FORM			EYE COLOR		HAIR COLOR			COMBINED HAIR-, EYE COLOR AND HEAD FORM				FOREIGN ORIGIN																								
	Blood group	Blood group numb. and percentage	Dolichocephalic	Mesocephalic	Brachycephalic	Brown and Grey-brown	Blue and Greyblue	Black	Dark blonde	Fair	Black hair Brown (gr. br.) Eye	Black hair Brown (gr. br.) Eye Brachycephalic	Fair hair Blue (gr. bl.) Eye	Fair hair Blue (gr. bl.) Eye Dolichocephalic	Jewish Origin	Foreign Origin	Scandinavian	Scottish	English	Irish	Belgian	German	Austrian	Swiss	French	Italian	Spanish	Portuguese	Ungarian	Finnish	Polish	Russian	Balcanese	Armenian	Indonesian	West Indian	Chinese	Siamese	Negro
O	Number	1411	155	667	589	526	726	122	712	542	90	45	395	38	63	760	18	13	30	1	46	322	5	17	151	9	16	2	4	1	4	7			46	1	3	1	
	Percentage of O		11.0	47.3	41.7	37.3	51.5	8.6	50.5	38.4	6.4	3.2	28.0	2.7	4.5	53.9						22.8			10.7										3.3				
	m		±0.84	±1.33	±1.31	±1.29	±1.34	±0.75	±1.33	±1.30	±0.66	±0.47	±1.21	±0.44	±0.54	±1.33						±1.13			±0.85										±0.48				
	Percentage of Total	45.7	45.5	44.9	46.7	44.0	47.1	47.6	45.7	45.2	44.3	47.9	46.4	44.7	44.4	48.1																							
	m	±0.91	±2.70	±1.29	±1.41	±1.44	±1.27	±3.12	±1.26	±1.44	±3.49	±5.15	±1.71	±5.39	±4.17	±1.26																							
A	Number	1270	130	637	503	498	628	85	644	513	69	27	349	31	58	610	13	9	24	3	48	239	6	13	132	7	8		3		7	5	2	1	26	4			1
	Percentage of A		10.2	50.2	39.6	39.2	49.4	6.7	50.7	40.4	5.4	2.1	27.5	2.4	4.6	47.3						18.8			10.4										2.0				
	m		±0.85	±1.40	±1.37	±1.37	±1.40	±0.70	±1.40	±1.37	±0.64	±0.41	±1.25	±0.43	±0.59	±1.39						±1.09			±0.86										±0.39				
	Percentage of Total	41.2	38.1	42.9	40.0	41.7	40.7	33.2	41.4	42.7	34.0	28.7	40.9	36.5	40.9	38.6																							
	m	±0.89	±2.63	±1.29	±1.38	±1.47	±1.25	±2.94	±1.25	±1.43	±3.33	±4.67	±1.69	±5.22	±4.13	±1.23																							
B	Number	297	38	138	121	129	126	35	148	107	34	17	71	9	12	145	5	3	1	1	12	45	1	2	35	3	5				1	2			16	1			
	Percentage of B		12.8	46.5	40.7	43.4	42.4	11.8	49.8	36.0	11.4	5.7	23.9	3.0	4.0	49.0						18.5			11.8										5.4				
	m		±1.94	±2.90	±2.85	±2.88	±2.87	±1.87	±2.90	±2.78	±1.84	±1.35	±2.47	±0.99	±1.14	±2.91						±2.25			±1.87										±1.31				
	Percentage of Total	9.6	11.1	9.3	9.6	10.8	8.2	13.7	9.5	9.0	16.7	18.1	8.3	10.6	8.4	9.2																							
	m	±0.53	±1.70	±0.75	±0.83	±0.90	±0.70	±2.15	±0.74	±0.83	±2.62	±3.97	±0.95	±3.34	±2.33	+0.73																							
AB	Number	107	18	42	47	41	62	14	53	38	10	5	37	7	9	65	2	1	1		1	27	3		11	1	3	1	1			1			3		1		
	Percentage of AB		16.8	39.3	43.9	38.3	57.9	13.1	49.5	35.5	9.3	4.7	34.6	6.5	8.4	60.7						25.2			10.3										2.8				
	m		±3.61	±4.73	±4.80	±4.70	±4.77	±3.28	±4.84	±4.62	±2.80	±2.05	+4.5	±2.4	±2.68	±4.72						±4.19			±2.9										±1.6				
	Percentage of Total	3.5	5.3	2.8	3.7	3.4	4.1	5.5	3.4	3.2	5.0	5.3	4.4	8.2	6.3	4.1																							
	m	±0.33	±1.21	±0.43	±0.53	±0.52	±0.51	±1.43	±0.46	±0.51	±1.53	±2.31	±0.70	±2.98	±2.04	±0.50																							
Total	Number	3085	341	1484	1260	1194	1542	256	1557	1200	203	94	852	85	142	1580	38	26	56	5	107	633	15	32	329	20	32	3	8	1	12	15	2	1	91	6	4	1	1
	Percentage	100	11.1	48.1	40.8	38.7	50.0	8.3	50.5	38.9	6.6	3.0	27.6	2.8	4.6	51.2						20.5			10.7										2.9				
	m		±0.56	±0.90	+0.88	±0.88	+0.90	+0.5	±0.90	±0.88	±0.45	±0.31	±0.80	±0.29	±0.38	±0.90						±0.72			±0.56										±0.29				

$p + q + r = 100.0$ $p = 25.6$ $q = 6.8$ $r = 67.6$

Moreover the students of dentistry and the veterinarians at Utrecht University come from every part. These branches of study are taught only at this University. Leiden University is represented by 360 medical students, Groningen by 165, Amsterdam by 223, Wageningen (Agriculture School) by 157, Nijmegen, Catholic University, only by 24 students. From Utrecht University 1349 persons, from Delft (the only Dutch University of technical science) 807 persons.

We will consider here this group of 3085 Dutch students as a whole.

The distribution of the blood groups is as follows:

O	*A*	*B*	*AB*
1411	1270	297	107
45.7 ± 0.91 %	**41.2** ± 0.89 %	**9.6** ± 0.53 %	**3.5** ± 0.33 %

Compared with other not yet published data in Holland, the percentage of *B* and *AB* proves to be higher in this group of students. This is especially the case, if one compares with most of the local investigations in rural districts. For comparison in fig. 4 the columns relating to the four blood

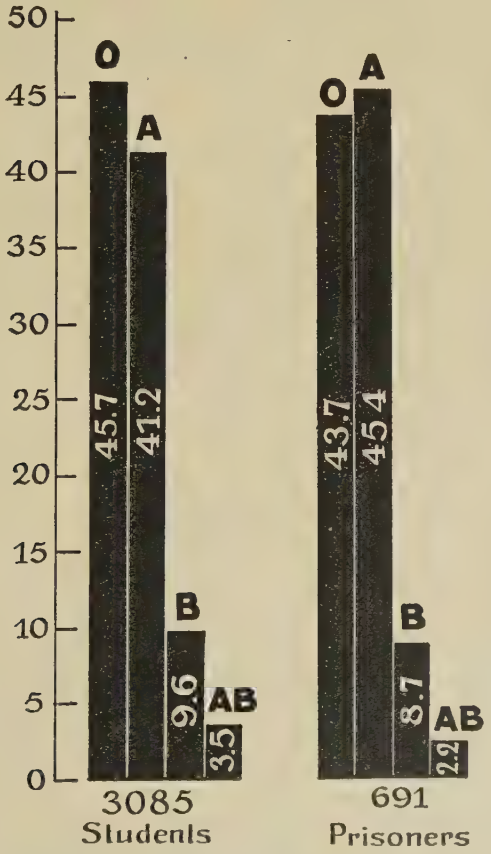

Fig. 4. Comparison between the blood group distribution amongst Dutch students and prisoners (in percentage).

groups of the students and those relating to a great number of prisoners (from the Netherland State Prisons) have been placed side by side. Though different social layers are represented in our students, most of them belong to a less sessile, more movable stratum of the population which has intermixed in the course of centuries with foreign elements. The proof is given by the remarkable high percentage of foreign descent, as indicated by the students (**51.2** ± 0.90 %).

Considering that there are many students who are not able to tell their grandparents' birth place — these **51.2** percent are still to be taken as minimum numbers. We are convinced that there exist a great many amongst them, who are unaware of the fact that one or more of their forefathers settled only in later centuries in our country.

From these 1580 students with foreign descent (father's, mother's side or from both sides), 633 that is **20.5** ± 0.72 percent have noted German origin; 329 that is **10.7** ± 0.56 percent French descent.

The blood group distribution of these 1580 persons as a whole is:

O	*A*	*B*	*AB*
48.1 ± 1.26 %	**38.6** ± 1.23 %	**9.2** ± 0.73 %	**4.1** ± 0.50 %

Expressed in percentages of the different blood groups as found in the entire group of 3085 students, one finds:

O	*A*	*B*	*AB*
760	610	145	65
53.9 ± 1.33 %	**47.3** ± 1.39 %	**49.0** ± 2.91 %	**60.7** ± 4.72 %

The countries of origin are noted in the table. Only for German and French origin the numbers are sufficiently high to compute a percentage. For German descent, expressed in percentages of the different blood groups, as found in the entire collection of 3085 students, one finds:

O	*A*	*B*	*AB*
322	239	45	27
22.8 ± 1.13 %	**18.8** ± 1.09 %	**18.5** ± 2.25 %	**25.2** ± 4.19 %

For French origin these figures are:

O	*A*	*B*	*AB*
151	132	35	11
10.7 × 0.85 %	**10.4** ± 0.86 %	**11.8** ± 1.87 %	**10.3** ± 2.9 %

142 (= 4.6 ± 0.38 %) students have noted jewish origin (partial or total). It is evident that these are also to be considered as minimum numbers. The percentage of the total number in every blood group is as follows:

O	*A*	*B*	*AB*
63	58	12	9
4.5 ± 0.54 %	4.6 ± 0.59 %	4.0 ± 1.14 %	8.4 ± 2.68 %

The mean error does not allow the conclusion that in this small group of jewish students, *AB* is represented more frequently than in the entire material. Still the undeniable high percentage of *AB*, in a group of more than 1000 Jews investigated in cooperation with us by Dr. H. HERTZBERGER, makes it quite probable that in our material the same is the case.

Indonesian origin is noted in 91 cases (also minimum numbers) = 2.9 ± 0.29 %. The distribution in the blood groups of the entire material is:

O	*A*	*B*	*AB*
46	26	16	3
3.3 ± 0.48 %	**2.0** ± 0.39 %	**5.4** ± 1.31 %	**2.8** ± 1.60 %

The number is too small to calculate the blood groups distribution of these 91 persons separately[1]. It may be said that the number 16 for blood group *B* is conspicuously high.

Amongst the 3085 students 433 belong to the female sex. The blood group distribution of the remaining 2652 male students is:

O	*A*	*B*	*AB*
1208	1090	256	98
45.6 ± 0.97 %	**41.1** ± 0.96 %	**9.6** ± 0.57 %	**3.7** ± 0.37 %

Comparing these figures with the percentages of the 3085 students together, it is evident that there is no reason to accept any difference in the blood group distribution amongst male and female in the material studied here.

The Eye colour.

For practical reasons only the contrast blue (resp. grey blue) and brown (resp. grey brown) are mentioned in the table. The remaining 349 persons are noted as grey-eyed. 1542 students that is **50.0** ± 0.90 percent were found to have blue (grey blue) eyes; 1194 that is **38.7** ± 0.88 percent to have brown (grey brown) eyes. For blue (grey blue) the distribution in every blood group of the entire students material is:

O	*A*	*B*	*AB*
726	628	126	62
51.5 ± 1.34 %	**49.4** ± 1.40 %	**42.4** ± 2.87 %	**57.9** ± 4.77 %

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[1] We tried in vain to investigate in Holland a larger number of persons of Indonesian descent. Several physicians had promised their assistance. Apparently in private praxis, even in Holland, this question encounters many difficulties. So the result has not been reached. Starting our investigation in Holland, we thought that it would be of great interest to state the influence of Indonesian mixture in the Dutch population by the study of the blood groups. It is known by the researches of BAIS and VERHOEF that the percentage of *B* and *AB* in the Dutch Indies is remarkably high. Continuing our work we found that in Holland the distribution of blood groups in different localities is so divergent that it will be impossible to state percentages for the country as a whole.

Our great interest in the study of the Indonesian influence as to the blood groups, for this reason somewhat diminished. This influence probably will only exist in larger town populations which for other reasons are avoided in our local investigations.

For brown (grey brown):

O	*A*	*B*	*AB*
526	498	129	41
37.3 ± 1.29 %	39.2 ± 1.37 %	43.4 ± 2.88 %	38.3 ± 4.70 %

In every group apparently more blue than brown eyes are found, except in group *B*.

As a separate group the 1542 students with blue (grey blue) eyes have the following percentage of blood group:

O	*A*	*B*	*AB*
47.1 ± 1.27 %	40.7 ± 1.25 %	8.2 ± 0.70 %	4.1 ± 0.51 %

The 1194 with brown (grey brown) eyes:

O	*A*	*B*	*AB*
44.0 ± 1.44 %	41.7 ± 1.47 %	10.8 ± 0.90 %	3.4 ± 0.52 %

The correlation between *A* → *B* and blue (grey blue) → brown (grey brown) eyes = + 0.050 ± 3 × 0.031.

This lays within the limits of 3 times the probable error. Therefore neither a positive nor a negative correlation can be said to exist between blood groups and eye colour in this group of 3085 students.

The Hair colour.

Amongst the 3085 students 1200, that is 38.9 ± 0.88 percent proved to be fair, 1557 = 50.5 ± 0.90 percent dark blonde; 256 = 8.3 ± 0.50 percent black haired (resp. very dark brown haired) 1) and 72 = 2.0 percent red haired.

The distribution over the 4 blood groups of the entire students material is:

I. For the fair haired:

O	*A*	*B*	*AB*
542	513	107	38
38.4 ± 1.30 %	40.4 ± 1.37 %	36.0 ± 2.78 %	35.5 ± 4.62 %

II. For the dark blonde:

O	*A*	*B*	*AB*
712	644	148	53
50.5 ± 1.33 %	50.7 ± 1.40 %	49.8 ± 2.90 %	49.5 ± 4.84 %

III. For the black haired:

O	*A*	*B*	*AB*
122	85	35	14
8.6 ± 0.75 %	6.7 ± 0.70 %	11.8 ± 1.87 %	13.1 ± 3.28 %

The apparently high percentage of the blackhaired in group *B* and *AB*

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1) As some of our collaborators have confused real black hair with darkest brown hair, this darkest brown also figures in the "black" column.

does not hold true when we take into account the average error. The correlation between blood group $A \rightarrow B$ and fair haired → black haired $= + 0.11 \pm 3 \times 0.036$. We hardly dare to speak in this latter case (where only the darkest hair pigment has been taken in account) of a positive correlation, though there certainly is a slight indication in this direction.

The students with light coloured hair and blue (grey blue) eyes are compared with the dark haired and brown (grey brown) eyed students. It appears that amongst 3085 students the first combination has been stated 852 times (= 27.6 ± 0.80 percent), the second combination 203 times (= 6.6 ± 0.45 percent).

Expressed in the percentage of the different blood groups of the entire material one finds:

I. For the combination light (fair) hair, blue (grey blue) eye:

O	*A*	*B*	*AB*
395	349	71	37
28.0 ± 1.21 %	**27.5** ± 1.25 %	**23.9** ± 2.47 %	**34.6** ± 4.5 %

II. For the combination dark pigmented hair, brown (grey brown) eyes:

O	*A*	*B*	*AB*
90	69	34	10
6.4 ± 0.66 %	**5.4** ± 0.64 %	**11.4** ± 1.84 %	**9.3** ± 2.80 %

Considered as separate groups the percentages of blood groups are:
For the combination light hair, blue (grey blue) eyes:

	O	*A*	*B*	*AB*
I.	**46.4** ± 1.71 %	**40.9** ± 1.69 %	**8.3** ± 0.95 %	**4.4** ± 0.70 %

For the combination dark pigmented hair, brown (grey brown) eyes:

	O	*A*	*B*	*AB*
II.	**44.3** ± 3.49 %	**34.0** ± 3.33 %	**16.7** ± 2.62 %	**5.0** ± 1.53 %

As one readily observes, the combination II reaches a high percentage for blood group *B*, as compared with that of the entire students material.

The correlation between blood group $A \rightarrow B$ and fair hair, blue (grey blue) eye → dark pigmented hair, brown (grey brown) eye $= + 0.16 \pm 3 \times 0.043$. So there is apparently a slight positive correlation, pointing to a higher frequency of a dark pigmentation of hair and eyes together in blood group *B* as compared to blood group *A*.

The Index cephalicus.

Amongst the 3085 students 341 = **11.1** ± 0.56 percent are dolichocephalic, 1484 = **48.1** ± 0.90 percent are mesocephalic and 1260 = **40.8** ± 0.88 percent have been found to be brachycephalic 1)). The preponderance

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1) Dolichocephaly I. C. < 76; Mesocephaly I. C. 76—81; Brachycephaly I. C. > 81.

of mesocephalic and brachycephalic over dolichocephalic in our material is very prominent. This is also the case, when only the male students are taken into account, the percentage of dolichocephaly remaining unaltered (11.3 ± 0.61 percent), the percentage of mesocephalic and brachycephalic changing respectively from 48.1 to 49.0 percent and from 40.8 to 39.7 percent. Nearly four times as many brachycephalic as dolichocephalic are found. The measurements have been taken by schooled assistents. Former investigators have already demonstrated the preponderance of brachycephaly in the Netherland population[1]).

We thought it worth while to investigate, whether perhaps the relatively large contingent of medical students from the southern provinces Limburg and Brabant at Utrecht University, might be responsible for the high percentage of brachycephaly. Therefore the figures of Delft and Utrecht University have been calculated separately. It appeared that for Delft 38.0 ± 1.7 percent of the students, for Utrecht 42.9 ± 1.36 percent had an Index cephalicus higher than 81. The difference is smaller than three times the probable error. The distribution over the four blood groups of the entire student material is as follows:

For Dolichocephaly:

O	*A*	*B*	*AB*
155	130	38	18
11.0 ± 0.84 %	10.2 ± 0.85 %	12.8 ± 1.94 %	16.8 ± 3.61 %

For Mesocephaly:

O	*A*	*B*	*AB*
667	637	138	42
47.3 ± 1.33 %	50.2 ± 1.40 %	46.5 ± 2.90 %	39.3 ± 4.73 %

For Brachycephaly:

O	*A*	*B*	*AB*
589	503	121	47
41.7 ± 1.31 %	39.6 ± 1.37 %	40.7 ± 2.85 %	43.9 ± 4.80 %

In each blood group the percentage of brachycephaly is high if compared with that of dolichocephaly. Considering these different groups separately, the distribution of blood groups is:

For the 341 Dolichocephalic:

O	*A*	*B*	*AB*
45.5 ± 2.70 %	38.1 ± 2.63 %	11.1 ± 1.70 %	5.3 ± 1.21 %

For the 1484 Mesocephalic:

O	*A*	*B*	*AB*
44.9 ± 1.29 %	42.9 ± 1.29 %	9.3 ± 0.75 %	2.8 ± 0.43 %

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[1] L. BOLK, Proceedings of the Royal Academy of Sciences Vol. 23 p. 103, 1920.

For the 1260 Brachycephalic:

O	A	B	AB
46.7 ± 1.41 %	**40.0** ± 1.38 %	**9.6** ± 0.83 %	**3.7** ± 0.53 %

There does not exist any correlation between the index cephalicus and the blood group *A* or *B*. This correlation between *A* → *B* and Dolichocephaly → Brachycephaly = + 0.033 ± 3 × 0.035 %.

The combination black hair, brown (grey brown) eye and Brachycephaly has been noted 94 times amongst the 3085 students = 3.0 ± 0.31 %. The combination fair hair, blue (grey blue) eye and Dolichocephaly 85 times = 2.8 ± 0.29 %.

The distribution over the four blood groups of the entire material is as follows:

For the combination fair hair, blue (grey blue) eye and Dolichocephaly:

O	A	B	AB
38	31	9	7
2.7 ± 0.44 %	**2.4** ± 0.43 %	**3.0** ± 0.99 %	**6.5** ± 2.4 %

For the combination black hair, brown (grey brown) eye and Brachycephaly:

O	A	B	AB
45	27	17	5
3.2 ± 0.47 %	**2.1** ± 0.41 %	5.7 ± 1.35 %	**4.7** ± 2.05 %

The correlation between blood group *A* → *B* and the combination fair hair, blue (grey blue) eye, Dolichocephaly → black hair, brown (grey brown) eye, Brachycephaly = + 0.17 ± 3 × 0.106.

This indicates that in this case as in the other a correlation is non existant.

In the litterature some investigations have described a positive correlation between blood group *B* and brachycephaly. If we limit ourselves to the investigations with a sufficient large material, it appears that H. OSTHOFF and W. KLEIN [1]) in the district Herne (Westphalen) found a remarkable high frequency of blood group *B* amongst brachycephalic in comparison with dolichocephalic. On the contrary O. STRENG [2]) in Helsingfors and his pupils, for Finland did not succeed in finding any correlation between blood group and index cephalicus. The same has been the case with our Dutch student material.

Even if originally there existed relatively more dolichocephalic amongst the persons belonging to blood group *A*, every crossing with a brachycephalic person of blood group *B* gives the chance that not only with the factor *B*, but as well with the factor O of a heterozygote *BO* brachycephaly is introduced in a person belonging phaenotypically to group *A*. The same holds for the relation between blood group and pigmentation. It has often been overlooked that anthropology is concerned with the phaenotype and not with the genotype. Now the blood group, as well as the hair colour and eye colour, offer the advantage that they are not appreciably modified by ambient circumstances, as seems to be possibly the case with the head-index [1]). But also in the latter material heterozygotes are not recognizable from homozygotes.

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[1]) Arch. f. Rassen- und Gesellschaftsbiologie. Bd. **17**, 1926. S. 371.

[2]) O. SIEVERS. Studier över Isoagglutinationen. Helsingfors 1927. A. K. VUORI. Die Vererbung d. Blutgruppen und deren Korrelation zu andern Eigenschaften. Helsingfors 1929. Acta soc. med. Fennicae "Duodecim". XII 1929.

In our population of 3085 students we find a slight indication of a positive correlation between blood group *B* and a darker pigmentation of hair and eye together. We should however like to postpone definite conclusions until the entire Dutch material collected by us, has been tested in this direction [2]).

Following BERNSTEIN's terminology the probability of the agglutinogenes *A*, *B* and *O* of the red blood corpuscules is respectively called *p*, *q* and *r*. For the 3085 students one finds:

$$\begin{aligned} p &= 25.6 \\ q &= \ \ 6.8 \qquad p + q + r = 100. \\ r &= 67.6 \end{aligned}$$

It might be, that afterwards in litterature the blood group relation of these 3085 Dutch students will be introduced in the card of O. STRENG (three axes, representing *p*, *q* and *r*) [3]) or in its modification by HIRSZFELD (three axes representing *A*, *B* and *O*). In that case however, it should not be overlooked, that these figures do not represent the blood group distribution of the Dutch nation. We shall probably never be able to enter Holland as a whole in these schemes.

Summary.

3085 students from different parts of Holland have been tested as to their blood group. In the same time a number of other anthropological traits have been noted. The percentage of the *B* group proves to be higher than generally has been found during our local investigations in several rural districts. This is ascribed to the fact that these students, though representing different layers of the Dutch society, have to be considered *in toto* as a group of mixed origin. This has been affirmed by the large percentage of persons with partially foreign origin.

For a comparison the distribution of the blood groups amongst prisoners,

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[1]) The age of the students excludes practically the possibility of changing of hair colour. So it may be excluded that in this material persons are qualified to be fair haired, who ought to be considered to belong to the dark pigmented hair type.

[2]) It might be possible, that the students with Indonesian origin are responsible for this positive correlation. In the investigation of the rural districts we are able to avoid this factor.

[3]) Eine Völkerkarte. Acta Soc. Med. Fennicia „Duodecim" VIII 1926.

belonging for the greater part to the more sessile layers of our population, has been chosen (fig. 4).

So it has been proved again by this investigation of a large number of students, that the pure population of a country is not represented by any, even spaciously selected intellectual part of society, but has to be sought in local rural districts. The results of the local investigations will be published in following Proceedings.

A correlation between index cephalicus and blood group lacks in our material. The correlation between dark pigmented eye colour and group *B* also falls within the probable error. Only a slight positive correlation exists, if one compares the frequency of blood group *B* with the dark pigmentation of hair and eye together. It has to be awaited whether this result will be confirmed by the study of the larger Dutch material, which has been collected by us in the last 4 years.

The collecting of the material in some Universities has been performed by collaborators. We especially have to thank Miss W. KEERS, biologist, for her organisatory work at Delft. As to the elaboration of the data we had the valuable assistance of Mr. F. SCHRIJVER, med. doct. at Utrecht University.

The agglutinations of the investigations published in this paper, are without exception performed by us personally and tested twice.